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CHEMISTRY

GENERAL, MEDICAL, AND PHARMACEUTICAL

At the First International Pharmaceutical Exhibition held in Vienna in August 1883, *for this Manual the Author was awarded a Gold Medal. At the Second, held in Prague in* 1896, *he received for the book the still higher, indeed the highest, prize of a Diploma of Honour.*

CHEMISTRY

GENERAL, MEDICAL, AND PHARMACEUTICAL

INCLUDING THE

CHEMISTRY OF THE BRITISH PHARMACOPŒIA

A MANUAL

ON THE SCIENCE OF CHEMISTRY, AND ITS APPLICATIONS
IN MEDICINE AND PHARMACY

BY JOHN ATTFIELD, F.R.S.

M.A. AND PH.D. (TÜBINGEN), F.I.C., F.C.S.

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ONE OF THE THREE EDITORS OF THE BRITISH PHARMACOPŒIA, 1885;
EDITOR OF THE ADDENDUM TO THE BRITISH PHARMACOPŒIA,
1890; EDITOR OF THE BRITISH PHARMACOPŒIA, 1898, AND OF
ITS INDIAN AND COLONIAL ADDENDUM, 1900

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EIGHTEENTH EDITION

LONDON
GURNEY & JACKSON, 1 PATERNOSTER ROW
1903

"But the greatest error of all is, mistaking the ultimate end of knowledge; for some men covet knowledge out of a natural curiosity and inquisitive temper; some to entertain the mind with variety and delight; some for ornament and reputation; some for victory and contention; many for lucre and a livelihood; and but few for employing the Divine gift of reason to the use and benefit of mankind."—LORD BACON.

"I hold that the greatest friend to man is labour; that knowledge without toil, if possible, were worthless; that toil in pursuit of knowledge is the best knowledge we can attain; that the continuous effort for fame is nobler than fame itself; that it is not wealth suddenly acquired which is deserving of homage, but the virtues which a man exercises in the slow pursuit of wealth; the abilities so called forth, the self-denials so imposed; in a word, that Labour and Patience are the true schoolmasters on earth."—LORD LYTTON.

"I want to learn all that one human being can. It is awful to be buried alive in the coffin of one's own ignorance and helplessness."—GRAHAM TRAVERS.

NOTE BY THE AUTHOR

The advance of years has obliged the Author, for the first time, to seek the collaboration of an Editor, and in Dr Leonard Dobbin he has had the good fortune to find a colleague whose knowledge of the science of chemistry and its general applications to medicine and pharmacy, and whose enthusiasm were commensurate with the labour involved. Occasional personal consultations, much correspondence, and the critical reading, by each, of every page of the "proofs" and "revises" of the text, have brought Author and Editor into entire agreement. The outcome must be left to the judgment of those for whom the edition has been prepared.

NOTE BY THE EDITOR

In undertaking the task of editing the Eighteenth Edition of this Manual it was necessary to act on certain broad principles. The most important of these were the following: 1. To preserve as far as possible those distinguishing features which have proved to be acceptable to those who use the book, as evidenced by the popularity it has enjoyed for a period of thirty-six years. 2. To bring the Manual into accord with the progress of chemical science since the previous edition was published. 3. To bear in mind the special needs of the constituency for whose instruction and reference the book is intended.

The Editor desires to express his best thanks to Dr B. Moore of Liverpool University, who kindly undertook the revision of the sections on certain proximate constituents of animal organisms and on the examination of urine and calculi; also to Dr Alex. D. White for constant assistance, and to Mr James Kerr, B.Sc., for occasional assistance in proof-reading and revision.

PREFACE

Adapted from the Prefaces of Previous Editions

The short title on the back of a book, and even the words on the title-page, are generally, and even necessarily, imperfect descriptions of the contents, and hence not infrequently induce at the outset misconceptions in the minds of readers. The author of "Chemistry: General, Medical, and Pharmaceutical" would at once state, therefore, that his chief aim has always been to teach the science of chemistry to medical and pharmaceutical pupils. So far as laws and principles are concerned, the book is a work on General Chemistry; but inasmuch as those laws and principles are elucidated and illustrated by that large portion of chemistry which is directly interesting to medical practitioners and pharmacists, the book may be said to be a work on Medical Chemistry and on Pharmaceutical Chemistry. Only in this conventional sense would the Author speak of Medical and Pharmaceutical Chemistry; for the truths of chemistry are the same for all students—crystalline verities which cannot be expanded or compressed to suit any class of workers. The leading principles of the science, however, can as easily be illustrated by or deduced from those facts which have interest as from those which have little or no special interest for the followers of medicine and pharmacy. The grand and simple leading truths or laws of chemistry, the lesser truths or principles, and nearly all the interesting relationships of elements and compounds, in a word, the *science* of chemistry, can be taught to medical and pharmaceutical students with little other aid than that afforded by the materials which lie in rich abundance all around these workers. Such a mode of teaching the general principles of the science, and their applications in medicine and pharmacy, is adopted in this volume. It is a mode which greatly increases the usefulness of the science to the students chiefly addressed, while it in no way diminishes the value of chemistry to them as an instrument of mental culture—an instrument which sharpens and expands the powers of observation, which enlarges and strengthens memory and imagination, which gives point to the perceptive faculties, and which develops and elaborates the powers of thought and of reason.

This Manual is intended, then, as a systematic exponent of the science of chemistry, but is written mainly for the pupils, assistants, and principals engaged in medicine and pharmacy. It is a Manual of Applied Chemistry, or Technical Chemistry, but it is first of all a Manual of Chemistry.

The book will be found equally useful as a reading-book for students having no opportunities of attending lectures or performing experiments, or, on the other hand, as a text-book for college pupils; while its comprehensive Index, containing some ten thousand references, will fit the work for after-consultation in the course of business or professional practice.

From most other chemical text-books it differs in three particulars:—first, in the exclusion of matter relating to compounds which at present are only of interest to the scientific chemist whose aims have no special relation to medicine and pharmacy; secondly, in containing more or less of the chemistry of every substance recognised officially, or in general practice, as a remedial agent; thirdly, in the paragraphs being so cast that the volume may be used as a guide in studying the science experimentally.

The order of subjects is that which, in the Author's opinion, best meets the requirements of medical and pharmaceutical students in Great Britain, Ireland, India, the British Colonies, and the United States of America. Introductory pages are devoted to a few leading properties of the elements. A review of the facts thus unfolded affords opportunity for stating the views of philosophers respecting the manner in which these elements influence each other as components of terrestrial matter. The consideration in detail of the relations of the elementary and compound radicals follows, synthetical and analytical bearings being pointed out, and attention frequently directed to connecting or underlying truths or general principles. The chemistry of substances met with in vegetables and animals, or of similar substances artificially produced (the so-called "organic chemistry"), is next considered. Chemical toxicology and the chemical as well as microscopical characters of morbid urine, urinary sediments, and calculi are then given. The concluding sections form a laboratory-guide to beginners in the study of quantitative analysis. In the Appendix is a table of the saturating-powers of acids and alkalies, designed for use in prescribing and dispensing, and an alphabetical list of elements with their atomic weights.

In the course of the treatment outlined in the preceding paragraph, it will be observed that the whole of the elements are first noticed very shortly, to give the student a general view of his course of study, and afterwards at length and thoroughly; that the chemistry of the metallic radicals precedes that of the acid radicals (a term applied consistently throughout the Manual to designate that part of each of the acids which is not replaceable hydrogen); and that while the metallic radicals are arranged according to their analytical relations, the common acid radicals are arranged according to exchangeable value or quantivalence, and the rarer acid radicals alphabetically. By this plan the more important facts and principles are repeatedly brought under consideration, the points of view, however, differing according as interest is concentrated on physical, synthetical, analytical, or quantitative properties. This arrangement of matter was adopted, also, partly in the belief that the separate and general truths of chemistry never do or can enter the mind in the order of any scientific classification at present possible. Chemical facts are not yet united by any single, consistent theory. In the current state of chemical knowledge, consistency in the methodical arrangement even of elements can only be carried out in one direction, and is necessarily accompanied by inconsistencies in other directions—a result most perplexing to learners, and hence totally subversive of the chief advantage of classification. For this reason the writer has preferred to lead up to, rather than follow, scientific classification—has allowed analogies and affinities to suggest, rather than be suggested by, classification. Among the acid radicals, especially, any known system of classification would have given undue prominence to one set of relations, and undeserved obscurity to others. Then, by separating more important from less important matter, instruction is adapted to the wants of readers whose opportunities of studying chemistry vary greatly, and are unavoidably insufficient to enable them to gain a knowledge of the whole area of the science. One great advantage of the mode of treatment is, that difficulties of nomenclature, notation, chemical constitution, and even those arising from conventionality of language, are explained as they arise, instead of being massed under the head of "Introductory Chapters," "Preliminary Considerations," or "General Remarks," which are not infrequently too difficult to be understood by a beginner, too voluminous to be remembered except by the aid of subsequent lessons, and are consequently the cause of much trouble and confusion. This plan has also admitted of greater prominence being given to "The General Principles of Chemical Philosophy," the only section to which the student is asked frequently to return until he finds himself naturally employing those principles in the interpretation of the phenomena obtained by experiment.

The metric system of weights and measures (that which, doubtless, is destined to supersede all others) is alone used in the sections on quantitative analysis. In other parts of the

Manual avoirdupois weights and imperial measures are employed, necessarily.

It is hoped that the numerous etymological references scattered throughout the following pages will be found useful. Words in Greek continue to be rendered, by special request, in English characters, letter for letter. The word "official" is used throughout for things recognised officially by the compilers of Pharmacopœias.

Students are strongly recommended to test their progress by frequent examination. To this end appropriate questions are appended to each subject.

The Author's ideal of a manual of chemistry for medical and pharmaceutical students is, then, one in which not only the *science* of chemistry is taught, but in which the chemistry of every substance having interest for the followers of medicine and pharmacy is noticed at more or less length in proportion to its importance, and at least its position in relation to the leading principles of chemistry set forth with all attainable exactness. The extent to which he has realised this ideal he leaves to others to decide. Such a work will doubtless in certain parts partake of the character of a dictionary; but this is by no means a fault, especially if a good index be appended; for the points of contact between pure and applied chemistry are thus multiplied, and abundant outlets supplied, by which a lover of the science may pass into other chemical domains by aid of other guides, or even into the regions of original research. Among the rarer alkaloids, bitter bodies, glucosides, salts of organic radicals, solid fats, fixed oils, volatile oils, resins, oleo-resins, gum-resins, balsams, and colouring-matters mentioned in this volume, will be found many such points whence the ardent student may start for the well-known, the less-known, or the untrodden paths of scientific chemistry.

WATFORD, HERTS,
1st September 1903.

LIST OF PREVIOUS EDITIONS

No. of Edition.	Date.	Notes.
1	1867	A hand-book of practical chemistry only.
2	1869	This and succeeding editions included the chemistry of the British Pharmacopœia.
3	1870	American edition; adapted to the United States Pharmacopœia.
4	1872	English edition.
5	1873	American edition.
6	1875	English edition. This and succeeding editions contained notices of substances included in the Indian Pharmacopœia.
7	1876	American edition.
8	1879	English editions.
9	1881	
10	1883	American edition.
11	1885	English edition.
12	1889	American edition.
13	1889	English edition.
14	1893	American edition.
15	1893	English edition.
16	1898	American edition.
17	1898	English edition.

ADVICE TO STUDENTS RESPECTING THEIR OBJECT IN STUDYING

Avoid studying chemistry, or indeed any subject, *merely* by way of "preparation for examination"; all ordinary "examinations" being, admittedly, inefficient tests of competency. Do not so mistake the means for the end. You are studying to fit yourself for your position in the world. Work diligently, study thoughtfully and deliberately; above all, be thorough; otherwise your knowledge will be inaccurate and transient, and will be unaccompanied by that enlightenment of the understanding, that mental training, mental discipline, and general elevation of the intellect which constitute, in a word, education. When you are thus educated, you will with ease and pleasure pass any examination in the knowledge you have thus acquired.

All authorities on education, whether statesmen, teachers, or examiners, regard "Examination," even by the most highly skilled "Board," with ample time at its disposal and a wide area from which to select questions, as but a partial test of knowledge, and an imperfect test of education. It is the least unsatisfactory, however, that has been devised, and is especially useful when, following instead of leading education, it is restricted to the subjects of a well-defined, earnestly followed, compulsory public curriculum of study—a curriculum directed by a competent representative body, administered by properly qualified teachers, and followed by pupils who have had sound preliminary training.

Students! in all honour and in the highest self-interest, take care that any inefficiencies inseparable from "examination" are abundantly compensated by the extent and precision of your knowledge, and by the soundness and thoroughness of your whole education.

APPARATUS

LIST OF APPARATUS FOR EXPERIMENTS IN ANALYSIS

List of Apparatus suitable for the three months' course of practical chemistry in the summer session of medical schools, or for any similar series of lessons—including the preparation of elementary gases, analytical reactions of common metallic and acid radicals, analysis of single salts, chemical toxicology, and the examination of urine, urinary sediments, and calculi :—

One dozen test-tubes.
Test-tube stand.
Test-tube cleaning-brush.
A few pieces of glass tubing, 8 to 16 in. long, with a few inches of indiarubber tubing to fit.
Small flask.
Two small beakers.
Two small funnels.
Two watch-glasses.
Two or three glass rods.
Wash-bottle.
Small pestle and mortar.
A 2-pint earthenware basin.
A 2-inch and a 3-inch evaporating basin.
Two porcelain crucibles.
Blowpipe.
Crucible tongs.
Round file.
Triangular file.
Small retort-stand.
Sand-tray.
Wire triangles.
Platinum wire and foil.
Test-papers.
Filter-paper.
Towel.
Two dozen corks.

(*This set, packed in a case, can be obtained of any chemical-apparatus maker for* 12*s.* 6*d. to* 15*s.*)

LIST OF APPARATUS FOR EXPERIMENTS IN SYNTHESIS AND ANALYSIS

A larger set, suitable for the performance of most of the synthetical as well as the qualitative analytical experiments described in this Manual :—

A set of evaporating-basins, of the following sizes :—
    One each 8½-inch, 7¼-inch, 6½-inch, 4-inch ; two 3-inch.
One retort-stand with clamp and three rings.
Two test-glasses.
One half-pint flask.
Half a quire of filter-paper.
Two porcelain crucibles.
One measure-glass, 5 oz.
Blowpipe, 8-inch.
Two glass funnels.
One doz. test-tubes (hard glass).
One test-tube brush.
One test-tube stand.
One pair of 8-inch brass crucible tongs.
Two soup-plates.
One flat-plate.
Two spatula knives.
One pair of scissors.
One round file.
One triangular file.
Half a pound of glass rod.
Half a pound of glass tubing.
One foot of small indiarubber tubing.
Three doz. corks of various sizes.
Platinum wire and foil.
Test-papers.
A nest of three beakers.

(*This set, packed in a case, can be obtained of any chemical-apparatus maker for* 25*s. to* 30*s.*)

A sponge, towels, and a note-book may be included.

LIST OF FURNITURE OF A CHEMICAL LABORATORY

The following apparatus should be ready to hand for students following an extended course of practical chemistry, in a room set apart for the purpose :—

A bench or table and stool.
Water-supply and sink.
A cupboard attached to a chimney with an outward draught.
A furnace fed with coke ; tongs, hot-plate or sand-bath, etc.
A waste-box.
Shelves for chemical and other materials in jars or bottles.
Gas-supply and lamp with flexible tube (or a spirit-lamp and spirit).
Iron stand or cylinder for supporting large dishes.
Iron adaptors for fitting dishes to cylinder.
Pestle and mortar, 5 or 6 inches.
One 6-inch funnel.
Twenty-eight test-bottles, 6-oz.
Also, in absence of water-supply and sink, brown pan, 1 or 2-gallon ; white jug, 1-gallon ; water-bottle, quart.

Other articles, such as flasks, retorts, receivers, condensers, large evaporating-dishes, may be obtained as wanted. In Quantitative Analysis the apparatus described in the sections on that subject will be required.

LIST OF FLUID REAGENTS

Certain chemical substances are used so frequently in analytical processes that it is desirable to have small quantities placed in bottles in front of the operator (*see* page 8). As these reagents are generally employed in a state of solution, nearly all the solid salts may at once be dissolved (in distilled water). The bottles employed should be well stoppered, and of 5 or 6 ounces capacity. Common glass bottles of this size may be had for about four shillings per dozen. The bottles should not be more than about three-quarters full ; single drops, if required, can then be poured out with ease and precision. The following list of test-solutions is recommended ; directions for methods of preparing the substances not readily purchasable will be found by referring to the Index :—

Sulphuric Acid, conc. and dilute.
Nitric Acid, ,, ,,
Hydrochloric Acid, ,, ,,
Acetic Acid, dilute.
Caustic Potash, 5 per cent. or B.P.
,, Soda, 5 to 15 per cent.
Ammonia, saturated and dilute.
Lime-water, saturated.

The following may contain about 10 per cent. of dissolved salt :—

Ammonium Carbonate, with a little solution of Ammonia added.
Ammonium Chloride.
Ammonium Phosphate.
Ammonium Hydrosulphide.
Barium Chloride.
Calcium Chloride.
Potassium Chromate.
Sodium Bitartrate.

ERRATA

Page 373, line 3 from bottom, *for* "one-half" *read* "one-fourth."
,, 390, lines 9 and 10 from top, *for* "myrobalanus" *read* "myrobalans."

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CHEMISTRY

GENERAL, MEDICAL, AND PHARMACEUTICAL

INTRODUCTION *

MAN can neither create matter nor destroy matter, but he can permanently alter its character. All that is burned is thus altered, and nearly all that is eaten and digested is thus altered. Man can in many cases bring about, or in a measure control, these permanent alterations which matter is capable of undergoing; and in all cases he can investigate the alterations in matter which are ever proceeding around him in animal, vegetable, and mineral nature. The study of these alterations in all their known length, and breadth, and depth, is the study of natural science, of which Chemistry—the study of most of the alterations—is one of the most comprehensive branches.

The infinite varieties of solid, liquid, and gaseous matter of which our earth and atmosphere are composed may be so altered by man as to be resolved into a few distinct substances appropriately termed Elements (*Elementum,* first or constituent principle of anything), for by no known means can they be further decomposed. More than seventy of these elements have been proved to exist. Some, such as gold, occur naturally in the uncombined state; but the greater number are combined in so subtle a manner as to conceal them from ordinary methods of observation. Thus none of the common properties of water indicate that it is composed of two elements, both gases, but differing much from each other; nor can the senses of sight, touch, and taste, or other ordinary means of examination, detect in their concealment the three elements of which sugar is composed. The art by which these and all other compound substances are resolved into their elements is termed the art of Chemistry, a name derived possibly from the Arabic word *kamai*, to conceal.* The *art* of Chemistry also includes the construction of compounds from elements, the decomposition of compounds, and the conversion of substances of one character into others of different character. The *science* of Chemistry deals with the general principles or leading truths relating to the elements, and to the manner in which they severally combine; with the observation of the phenomena which accompany chemical combinations, interactions, and decompositions; and with the description of the general properties of the substances produced during these changes.†

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* Students using this book as a guide in following chemistry practically should read the first four pages, and then commence work by preparing oxygen. All students should read the prefatory pages, especially the page of "Advice to Students."

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* The idea that common metals contained valuable metals concealed within them was the one seed from which chemical knowledge mainly sprang. The men who endeavoured to find the secret of such concealment were appropriately termed *alchemists*, and their efforts were spoken of as *alchemy* (*al kimia*, from *kamai*, to conceal). Their persistent labours, generation after generation, were unsuccessful so far as the transmutation of baser metals into gold was concerned, yet were invaluable to posterity; for new substances were discovered and truths of nature unveiled: from these discoveries further discoveries resulted, and thus grew the still progressing branch of knowledge called Chemistry.

† Persons who practise the art and science of Chemistry are known as Chemists. Some two hundred or more years ago, and before Chemistry was a science, the only "Chemists" were the makers and vendors of chemical substances, used chiefly as medicines. They were the successors of the Alchemists. In Great Britain these chemists and the herb-dealers termed drug-grocers, otherwise druggists, gradually associated to form the "Chemist and Druggist." Between the "Chemist and Druggist" and the Physician there then existed the Apothecary—the putter together of medicines, or compounder of physicians' prescriptions. The Apothecary has since become a medical practitioner, prescriptions being now "made up"

From these few words concerning the nature of the art and science of chemistry, it will be seen that in most of the occupations that engage the attention of man, Chemistry plays an important part—in few more so than in the practice of the various departments of Medicine, especially the branches termed Therapeutics * and Pharmacy.†

Air, water, food, drugs, and chemical substances—in short, all material things—are composed, as stated, of Elements. An intimate knowledge of the properties of the more important Elements, both in the free (or uncombined) and in the combined state, and of the various substances they form when they have combined with each other; all attainable knowledge of the power or force (the chemical

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by the Chemist and Druggist. The latter in Great Britain, since the year 1868, has the title of *Chemist and Druggist*, his higher title being *Pharmaceutical Chemist*; these respective designations he legally assumes on passing the Minor and Major Examinations conducted by the Pharmaceutical Society of Great Britain, in accordance with the provisions of the Pharmacy Acts of 1852 and 1868. In Ireland, physicians' prescriptions are compounded by the *Pharmaceutical Chemist*, or Licentiate of the Pharmaceutical Society of Ireland. Other classes of Chemists are the Analytical Chemists, who give special attention to analysis; Manufacturing Chemists, who restrict their labours to the preparation of chemical substances; while others devote their knowledge and energies to Chemical Education or to Chemical Research, or are appealed to as Consulting Chemists by the persons, firms, corporations, or governments needing chemical advice respecting industrial processes, hygienic matters, etc. The callings of the Consulting and Analytical Chemist are generally united. Nearly all the leading professional Chemists in the United Kingdom are Fellows of the Institute of Chemistry of Great Britain and Ireland.

* Therapeutics (*θεραπευτικός*, *therapeutikos*, from *θεραπεύω*, *therapeuō*, I nurse, serve, or cure) is the branch of medicine which treats of the application of remedies for diseases. The therapeutist also takes cognisance of *hygiene*—the department of medicine which respects the preservation of health—and of *dietetics*, the subject of diet or food. By *pharmacology* is understood the normal or physiological action of drugs, as underlying the therapeutic action.

† Pharmacy (from *φάρμακον*, *pharmakon*, a drug) is the generic name for the operations of preparing or compounding medicines, whether performed by the Medical Practitioner or by the Pharmaceutical Chemist or the Chemist and Druggist. It is also sometimes applied, like the corresponding term Surgery, to the apartment in which the operations are conducted. *Pharmacognosy* is the study of the crude drugs of the vegetable and animal kingdoms.

force or chemical affinity) by which the elements contained in the compounds are held together; and the application of such knowledge to Pharmacy and Medicine, must be the objects sought to be attained by the student of chemistry for whom especially this book has been written.

The Elements.—Of the seventy or so known elements, the study of about forty is essential for the proper comprehension of chemistry. Fortunately for medical and pharmaceutical students all these are of special medical or pharmaceutical interest, hence such students while learning the science itself can study its applications to medicine and pharmacy. Two-thirds of the forty are metals, one-third non-metals. The remainder of the elements * are seldom met with in Nature, or occur only in small quantities; and a number of them have not received any practical application either in Medicine, Art, or Manufacture.

Before intimately studying the elements, it is desirable to acquire some general notions concerning them: such a procedure will also serve to introduce the practical student to his apparatus, and make him better acquainted with the various methods of manipulation.†

Metallic Elements.—With regard to the metallic elements, it may safely be assumed that the reader has sufficient knowledge for present purposes; but little, therefore, need be said respecting them at this stage. He has an idea of the appearance, relative weight, hardness, etc., of such metallic elements as gold, silver, copper, lead, tin, zinc, and iron. If he has not a similar knowledge of mercury, antimony, arsenium, platinum, nickel, aluminium, magnesium, potassium, and sodium, he should embrace the earliest opportunity of seeing and examining specimens of each of these metallic elements.

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* A list will be found in the Appendix. (*See* also pp. 26 and 52.)

† This allusion to apparatus need not discourage the youngest student of chemistry who is at the same time a pupil in medicine or pharmacy. With the aid of a few phials, wine-glasses, or other similar vessels, always at hand, he may, by studying the following pages, learn the chemical reactions which are constantly occurring in the course of making up medicines, understand the processes by which medicinal preparations are manufactured, and detect adulterations, impurities, or faults of manufacture. Among the substances used in medicine will be found nearly all the chemical materials required. If, in addition, a dozen test-tubes and a few feet of glass tubing be procured, many of the experiments described may be performed. For full lists of apparatus and chemical materials, see the prefatory pages.

Non-Metallic Elements.—With regard to the non-metallic elements, it is here supposed that the student has no general knowledge. He should commence his studies, therefore, by a series of operations as follows, on eight of their number.

OXYGEN

Preparation.—Oxygen is the most abundant element in nature, forming (in a state of combination) about one-half of the whole weight of our globe. To obtain it for experimental purposes all that is necessary is to apply heat to certain easily decomposable compounds containing oxygen, whereupon the latter is evolved in the gaseous condition. There are several substances which readily yield oxygen upon heating, but the crystalline salt known as potassium chlorate is perhaps best fitted for the experiment. The size and form of the vessel in which to heat the salt will mainly depend on the quantity of oxygen required; but for the purposes of the student the best is a *test-tube,* an instrument in constant use in studying practical chemistry. It is simply a tube of thin glass, a few inches in length, and half or three-quarters of an inch in diameter, closed by fusion at one end. It is made of thin glass, in order that it may be rapidly heated or cooled without risk of fracture. (*See* pictures of test-tubes in figures 3 and 4.)

Outline of the Process.—Heat potassium chlorate (say, as much as will lie on a shilling) in a test-tube held in the flame of a Bunsen burner or spirit lamp. The salt first fuses—*i.e.,* liquefies—and forms a colourless liquid; and, on further heating this liquid, gaseous oxygen is quickly evolved.

Before applying heat, however, provision should be made for collecting the gas.

Collection of Gases (*see* in fig. 3).—Procure a piece of glass tubing about the thickness of a quill pen, and a foot or eighteen inches long, and fit it to the test-tube by means of a cork. (Longer tubes may be neatly cut to any size by smartly drawing the edge of a triangular file across the glass at the required point, then clasping the tube, the scratch being between the hands, and pulling the portions asunder, the pull being exerted as if to open out the crack which the file has commenced.) The tube is fixed in the cork through a round hole made by the aid of a red-hot wire, or, better, by a rat-tail file, or, best of all, by one of a set of cork-borers—pieces of brass tubing of different diameters, sharpened at one end and having a flat head at the other. The cork and test-tube must be fitted to each other accurately and closely, but not so tightly as to break the test-tube. The long piece of tubing should be bent to the most convenient shape for delivering the gas.

To Bend Glass Tubes.—Hold the part of the tube required to be bent in any gas- or spirit-flame (a fish-tail gas-jet, for example, fig. 1), constantly rotating it, so that about an inch of the glass becomes heated. It will soon begin to soften, and by the *gentle* pressure of the fingers, it can then be made to assume any required angle. In the present case, the tube should be heated at about four inches from the extremity to which the cork is attached, and bent to an angle of 90 degrees (fig. 2). A similar bend may be made near the other end, and the short piece of straight

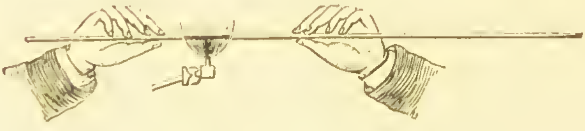

FIG. 1.—Softening and Bending Glass Tubes.

tubing at this end should then be cut off. The cut ends should finally be rounded off by holding them in the flame until the glass softens. The finished tube has the shape shown in fig. 3.

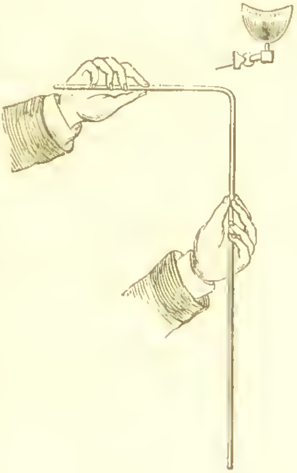

FIG. 2.

Collection of Gases (continued).—Fit the cork and bent tube into the test-tube; the apparatus will then be ready for delivering gas at a convenient distance from the heated portion of the arrangement. To collect the oxygen, have ready three or four test-tubes (or small wide-mouthed bottles) quite filled with water, and inverted in a basin or other vessel, also containing water, taking care to keep the mouths of the filled tubes a little below the surface. Now apply heat to the chlorate contained in the test-tube, and so arrange the open end of the bent tube under the water that the gas which presently escapes with effervescence from the melted chlorate may pass out from the free end of the tube, and may bubble into and gradually fill the previously water-filled inverted test-tubes. The first tubeful may be rejected, as it probably consists of little more than the air which was originally in the apparatus and has been displaced by the oxygen. That which comes afterwards will be practically pure oxygen.

As each tube or bottle becomes full, close its mouth (still under the surface of the water) by a cork and then set it aside; or instead of a cork a little cup (such as a porcelain crucible or small gallipot) may be brought under its mouth, and the cup, with the mouth of the tube in it, be lifted out of the water and placed aside until wanted, the water remaining in the cup effectually preventing the gas from escaping.

On the large scale, oxygen may be prepared in the same

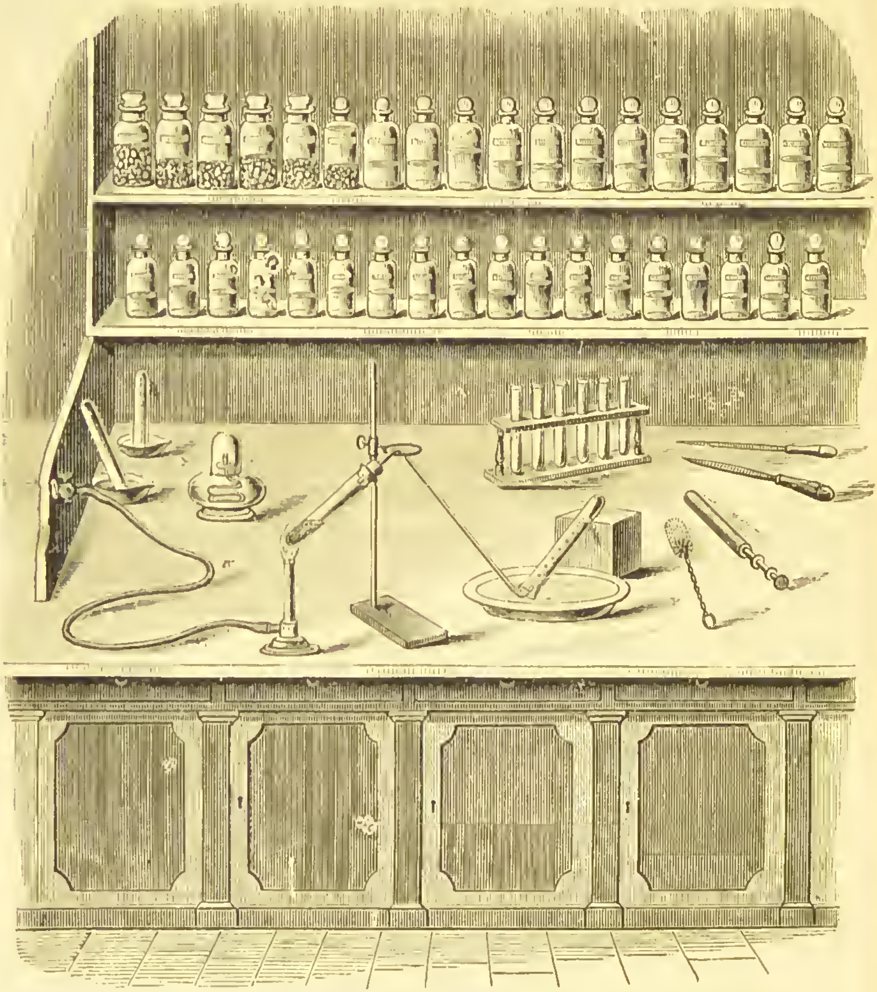

FIG. 3.—This picture represents the preparation, collection, and storage of small quantities of oxygen gas. A test-tube and bent glass tube, connected by means of a perforated cork, are supported by the arm of an iron stand. (The apparatus might be held by the fingers.) The test-tube is heated in a "Bunsen" flame. (The spirit-lamp shown at back might be used instead.) The gas evolved from the heated substance displaces water from an inverted test-tube. Spare tubes in a test-tube rack are at hand, and tubes already filled with the gas have been set aside till wanted. A set of cork-borers, a round file, a triangular file, and a test-tube cleaning brush are lying on the table or student's bench. Below are cupboards for apparatus, above are bottles containing testing liquids, etc.

way, larger vessels (glass flasks or iron bottles) being employed. If the potassium chlorate be previously mixed with about an equal weight of common black manganese oxide, the oxygen will be given off at a considerably lower temperature.

Oxygen, when required in a very pure state for medicinal purposes, might be prepared by adding water, in small successive quantities, to a mixture of sodium peroxide and sand; but the high degree of purity attained in the commercial preparation of oxygen from the atmosphere (by a method that will be described later) by manufacturers who supply the gas compressed in steel cylinders, renders this oxygen suitable for all such purposes.

Note on the Collection and Storage of Gases.—A number of gases, whether prepared for experimental purposes or on the large scale, may be collected and stored in vessels inverted in water in the manner just described for oxygen. Thus coal-gas (generated at gas-works by strongly heating coal in iron retorts, very much the shape of test-tubes, only as many feet long as a test-tube is inches) is stored in the well-known iron gas-holders which may be regarded as playing the part of the inverted test-tubes or bottles in the oxygen experiment. It is plain that collection and storage over water is only practicable in the case of gases which do not dissolve to more than a small extent in water. Coal-gas and other gases besides oxygen may be stored in steel cylinders under high pressure.

Solubility of Gases in Water.—All gases are more or less soluble in water. The quantity of any gas which dissolves depends upon the temperature—cold water dissolving more than hot—and upon the pressure. Whatever the quantity of a gas dissolved by a liquid at ordinary atmospheric pressure, double that quantity is dissolved at double the pressure, treble that quantity at treble pressure, and so on. This is a general law (Henry and Dalton) regarding the solubility of gases in liquids at constant temperatures.

Properties.—Free oxygen is a colourless, odourless, and tasteless gas. Cailletet and Pictet succeeded in liquefying it on a small scale, and Wroblewski and Olszewski obtained it in larger quantity as a transparent fluid, closely resembling water in appearance, but slightly bluer; Dewar has now liquefied it in large quantities, and has also obtained it in the solid condition. Obviously oxygen is not very soluble in water, or it could not be collected by the aid of that liquid. It is soluble, however, to a certain extent, about 3 volumes dissolving in 100 of water at ordinary temperatures. When any ordinary sample of cistern or river water is heated, or subjected to greatly reduced pressure, numerous small bubbles of gas, containing a considerable proportion of oxygen, gradually escape from it. The presence of dissolved oxygen in river and sea water is essential for the respiration of fishes.

To observe the relation of oxygen to combustion, remove one of the tubes from the water, by placing the thumb over its mouth, and apply for a second a lighted wood match to the orifice; the gas will be found to be incombustible. Extinguish the flame of the match, and then quickly introduce the still incandescent carbonised extremity of the wood well inside the test-tube; the wood will at once burst into flame, owing to the extreme violence with which oxygen supports combustion. These tests of the presence of free oxygen may also be applied at the extremity of the delivery-tube whilst the gas is being evolved. (It is desirable to retain two tubes of the gas for use in subsequent experiments; also one tube in which only one-third of the water has been displaced by oxygen.)

Relation of Oxygen to Animal and Vegetable Life.—Not only the carbon at the end of a piece of charred wood, but any other substance that will burn in air (which, as will be seen presently, is diluted oxygen) will burn more brilliantly in pure oxygen. The warmth of the bodies of animals is kept up by the continuous burning of the tissues in the oxygen of the air, drawn into the system through the lungs. The product of this combustion is exhaled into the air as a gaseous compound of carbon and oxygen termed carbonic anhydride, a gas which, in sunlight, is absorbed by and decomposed in the cells of plants with fixation of the carbon and liberation of the oxygen. Thus, too, is the atmosphere kept constant in composition.

Memorandum.—At present it is not advisable that the reader should trouble himself with the consideration of the chemical action which occurs either in the elimination of oxygen from its compounds, or in the separation of any of the following non-metallic elements from their combinations. It is to the properties of these elements themselves, especially in their free, or uncombined, condition, that he should at present restrict his attention. Working thus from simple to more complex facts, he will in due time find that the comprehension of such actions as occur in the preparation of these few elements will be easier than if he attempted their full study now.

HYDROGEN

Preparation and Collection.—The element Hydrogen, in the uncombined state, is also a gas.* It is obtainable from its commonest compound, water (of which about one-ninth by weight is hydrogen), by the agency of hot zinc or iron, but more conveniently by the action of either of these metals on cold *dilute* sulphuric acid. The apparatus used for making oxygen may be employed for this experiment; but no lamp is required. Place several pieces of thin zinc * in the generating tube (fig. 4), or in a common glass bottle (fig. 5) or flask, and cover them with water. The collecting-tubes (these also may be wide-mouthed bottles) being ready, add concentrated sulphuric acid (oil of vitriol) to the zinc and water, in the proportion of about 1 volume of acid to 5 of water, and fit on the delivery-tube; or pour the acid down such a funnel-tube † as is shown in fig. 5; the hydrogen at once escapes with effervescence from the fluid. Having rejected the first portions (or having waited until the air originally in the bottle may be considered to be all expelled), collect four or five tubes of the gas in the manner described under oxygen.

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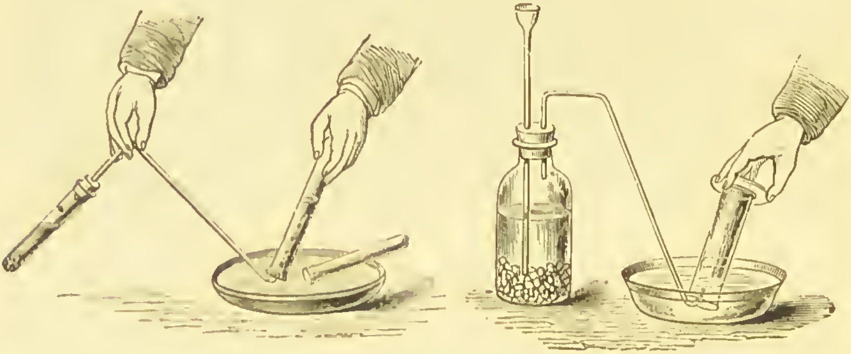
* Graham obtained alloys of hydrogen with palladium and other metals, compounds in which several hundred times its bulk of gas is retained by the metal *in vacuo* or even at a red heat. This was regarded as physical confirmation of the opinion long held by chemists, that hydrogen is a gaseous metal. Graham termed it *hydrogenium*, other chemists *hydrium*, and considered its relative weight in the solid state to be nearly three-fourths that of water. Olszewski claimed to have liquefied hydrogen in 1895. It has been liquefied by Dewar, who finds its critical temperature (*i.e.*, the temperature to which it must be cooled before it is possible to convert it into the liquid state by the application of any pressure, however great) to be approximately −233° C., and its boiling point −243° C.

Helium.—More than thirty years ago, Frankland and Lockyer, to account for a certain yellow line in the solar spectrum, assumed the existence of a separate element which they termed helium. In 1895 Ramsay found a new element in the mineral clevite giving on ignition a yellow line in the spectrum, probably identical with that just alluded to. To this new terrestrial element he gave the name helium. Ramsay, Collie, and Travers afterwards found helium in many minerals, often accompanied by hydrogen, though it seems rather to have analogies with argon, another new element which will be referred to under nitrogen. Many minerals yield gases when heated, and even contain gases in cavities.



Figs. 4 and 5.—Preparation of Hydrogen.

Notes.—In making larger quantities, bottles of appropriate size may be employed. Other metals, notably potassium and sodium, liberate hydrogen the moment they come into contact with water; but the processes are not economical, and the action is dangerously violent.

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* The best form is *granulated zinc* prepared by heating zinc in an iron ladle over a fire, and immediately the metal is fused, pouring it in a slow stream into a pail of water from a height of 8 or 10 feet. Each drop of zinc thus yields a thin little bell, which, for its weight, presents a large surface to the action of the acid liquid. If the melted zinc becomes too hot, the little bells will not be formed. A trace of iron in the zinc greatly increases the rate at which the hydrogen is evolved.

† Funnel-tubes may be purchased of the apparatus-maker; or, if the pupil has access to a table blowpipe, and the advantage of a tutor to direct his operations, they may be made by himself.

Properties.—Hydrogen, like oxygen, is colourless, odourless, and tasteless. If iron be used to generate the gas, it has a marked smell; but this is due to impurities derived from the iron.

Apply a flame to the mouth of the delivery-tube, but not until it is plain that the brisk effervescence of hydrogen must have resulted in the driving out of all air from the generating tube or bottle, *for the mixture of hydrogen and air may explode.* Ignition of the hydrogen ensues, showing that, unlike oxygen, it is combustible.

Plunge a lighted match well into a tube (or wide-mouthed bottle) containing free hydrogen; the gas is ignited, but the match becomes extinguished. This shows that hydrogen is not a supporter of ordinary combustion.

Hydrogen in burning unites with the oxygen of the air and forms water, which may be condensed on a cool glass or other surface. Prove this by holding a glass vessel a few inches above a hydrogen-flame. In burning the hydrogen contained in one of the tubes or bottles, the flame is best seen when the tube is held mouth upwards, and water poured in so as to expel the gas gradually.

If, instead of this gradual combination of the two elements oxygen and hydrogen, they be mixed together in the right proportions and then ignited, they will rapidly combine, and explosion will result. Prepare a mixture of this kind by filling up with hydrogen a test-tube from which one-third of the water has already been expelled by oxygen. Remove the tube from the water, placing a finger over its mouth, and having a lighted match ready, apply the flame; explosion ensues, owing to the instantaneous combination of the whole bulk of the two elements, and the expansive force of the highly heated steam produced. If anything larger than a test-tube is employed in this experiment, it should be an aërated water bottle, or some such vessel equally strong.

Notes.—These gases thus unite at a temperature far higher than that of boiling water, two volumes of hydrogen and one of oxygen yielding two of gaseous water (steam).

The noise of such explosions is caused by concussion between the suddenly expanded gaseous body and the air.

The force of the explosion, or, in other words, the pressure of the suddenly heated and therefore suddenly expanded steam, is below that necessary to break the test-tube. Some pressure, however, is exerted; and hence the necessity of the precaution previously suggested, of allowing all the air which may be in a hydrogen-apparatus to escape before proceeding with the experiments. If a flame be applied to the delivery-tube before all the air is expelled, the probable result will be ignition of the mixture of hydrogen and oxygen (of the air) and consequent explosion. But even in this case the generating vessel is not often fractured unless it be large and of thin glass, the ordinary effect being that the cork is blown out, and the delivery-tube broken on falling to the ground.

Hydrogen is a constituent of all the substances burned for producing artificial light, such as solid fats, oil, and coal-gas. The explosive force of large quantities, such as a roomful, of coal-gas and air is well known to suffice for blowing out that side of the room which offers least resistance.

The composition of water can be proved analytically as well as synthetically, by passing a current of electricity through dilute sulphuric acid (electrolysis, from λύω, *luo,* I loose, or I decompose). During the passage of the current, hydrogen and oxygen are liberated in the proportions in which they are present in water, twice as much hydrogen as oxygen, by volume, being produced. The quantity of sulphuric acid remains the same at the end as at the beginning of the experiment, the quantity of water having alone diminished.

Combustion (from *comburo,* I burn).—The experiments with hydrogen and oxygen illustrate the true character of combustion. Whenever chemical combination is sufficiently intense to be accompanied by heat and light, the materials are said to undergo combustion. Combustion only occurs at the line of contact of the combining bodies; a jet of oxygen will burn in an atmosphere of hydrogen quite as easily as a jet of hydrogen in oxygen. A jet of air (diluted oxygen) will burn as readily in a jar of coal-gas as a jet of coal-gas burns in air; each is combustible, each supports the combustion of the other. Hence the terms *combustible* and *supporter of combustion* are merely conventional, and only applicable so long as the circumstances under which they are applied remain the same. In the case of substances burning in air, the conditions are, practically, always the same; hence no confusion arises from regarding air as the great supporter of combustion, and bodies which burn in it as being combustible.

Structure of Flame.—A candle-flame (fig. 6) or oil-flame is composed of intensely heated material; the central portion is unburnt gas, the next envelope is formed of partially burnt and very dense gaseous and solid particles sufficiently highly heated to give light, and the outer cone of completely burnt gases. In the figure the sharpness of limit of these cones is purposely somewhat exaggerated. Air made by any mechanical contrivance to mix with the gas in the interior of a flame at once burns up, or perhaps prevents the formation of, dense gases; giving a hotter, but non-luminous jet. The air-gas lamps (fig. 7), or "Bunsen" gas-burners, commonly used in chemical laboratories, are constructed on this principle; their flame has the additional advantage of not yielding a deposit of soot.

Fig. 6.—Structure of Candle-flame.

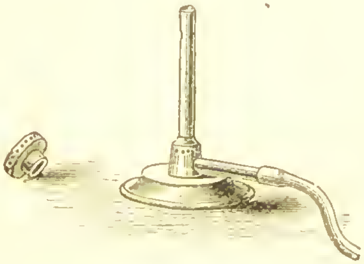


Fig. 7.—"Bunsen," or Air-gas, Burner.

In the air-gas burner coal-gas escaping from a small orifice at the bottom of the upright tube draws in and mixes with rather more than twice its volume of air (supplied through adjacent holes). The mixture, when kindled, only burns at the end of the upright tube, and not within it, partly because the metal of the burner, by conducting heat away, cools the mixture below the temperature at which it can ignite; partly because the velocity with which the mixture flows out is greater than the rate at which such a mixture ignites; and partly because the proportion of air to gas in the mixture is insufficient for perfect combustion, the external air immediately surrounding the flame contributing materially to the complete combustion of the gas. In the *Davy safety-lamp* advantage is taken of the rapidity with which a surface of wire gauze conducts away heat: a wire-gauze cage surrounds an oil-flame; an inflammable mixture of gas (fire-damp) and air can pass through the gauze and burn inside; but the flame cannot, ordinarily, be communicated to the mixture outside, because the metal of the gauze and of the other parts cools down the gas below the temperature at which combustion can continue.

Properties of Hydrogen (continued).—Gaseous hydrogen is the lightest substance known. It is used for filling balloons, but has been, to some extent, superseded by coal-gas because coal-gas, though not so light, is cheaper and more easily obtained. The lightness of hydrogen may be rendered evident by the following experiment:—Fill two test-tubes with the gas, and hold one with its mouth downwards and the other with its mouth upwards. The hydrogen will have escaped from the latter in a few seconds, whereas the former will still contain the gas after the lapse of many seconds. This may be proved by applying a lighted match to the mouths of the tubes.

The relative weight or specific gravity of oxygen is nearly sixteen times that of hydrogen. A vessel holding one grain of hydrogen will hold nearly sixteen grains of oxygen. The relation of the weight of hydrogen to air is as 1 to 14·44, or as 0·0693 to 1·0. One grain of hydrogen by weight measures about 27 fluid ounces, and, therefore, would about fill a common wine-bottle. Such a bottle would, at ordinary temperatures, hold about $14\frac{1}{2}$ grains of air, or about 16 grains of oxygen.

Mem.—It is desirable to retain two tubes of hydrogen for use in subsequent experiments.

Diffusion of Gases—Hydrogen cannot be kept in such vessels as the inverted test-tube of the above experiment; for, though much lighter than air, it *diffuses* downwards into the air, while the air, though much heavier, diffuses upwards into the hydrogen. This power of *diffusion* is possessed by all gases. The rates of diffusion of the different gases are inversely proportional to the square roots of the densities of the gases (*Graham*). Thus hydrogen diffuses four times faster than oxygen. This great and important property of diffusion suggests that the particles of gases are always moving, never at rest; how otherwise *could* gases diffuse into each other as they do, notwithstanding the opposing influence of gravitation? Diffusion strongly supports this (Clausius's) kinetic (*κῐνέω, kineō*, I move, or put in motion) theory of the physical condition of gases.

PHOSPHORUS

Appearance and Source.—Phosphorus (*Phosphorus*, B.P.) is a solid element, in appearance and consistence resembling white wax; but it gradually becomes yellow by exposure to light. It is a constant constituent of bones, and may be prepared from them by a process which will be described subsequently.

Caution.—Phosphorus, on account of its great affinity for oxygen, takes fire very readily in the air, and should therefore be kept under water. When wanted for use, it must be cut under water. It is employed in tipping lucifers, though *red* or *amorphous phosphorus* is less objectionable for this purpose.

Experiment.—Dry a piece of ordinary phosphorus, about one-fourth the size of a pea, by quickly and carefully pressing it between the folds of porous (filter or blotting) paper; place it on a plate, and ignite it by touching it with a piece of warm wire or wood. The product of combustion is a dense white suffocating smoke, which must be confined at once by placing an inverted tumbler, or beaker, or other similar vessel over the phosphorus. The fumes rapidly aggregate, and fall in white flakes on the plate. When this has taken place, and the phosphorus is no longer burning, moisten the powder with a drop or two of water, and observe that some of the water is converted into steam, an effect due to the intense affinity with which another portion of the water and the powder have combined, with the evolution of heat.

The powder produced by the combustion of phosphorus is termed phosphoric anhydride ; the combination of the latter with the elements of water produces a variety of phosphoric acid which dissolves in the water and forms, on standing, a dilute solution of ordinary phosphoric acid. The Diluted Phosphoric Acid of the "British Pharmacopœia" is a similar solution, made in a somewhat different way, and of definite strength.

NITROGEN

Source.—The chief source of this gaseous element is the atmosphere, nearly four-fifths of which consists of nitrogen (whilst roughly one-fifth is oxygen).

Preparation.—Burn a piece of dry phosphorus, the size of a pea, in a confined portion of air. The oxygen is thus removed, and the nitrogen remains. The readiest mode of performing this experiment is to fix a piece of earthenware (the lid of a small porcelain crucible answers very well) on a thin piece of cork, so that it may float in a dish of water (fig. 8). Place the dry phosphorus on the lid, ignite with a warm rod, and then invert a tumbler, or any glass vessel of about a half-pint capacity, over the burning phosphorus, so that the mouth of the glass may dip into the water. Let the arrangement rest for a short time, for the flakes of phosphoric anhydride to subside and dissolve in the water, and then decant the gas into test-tubes as indicated in fig. 9, using a tub or other vessel of water of sufficient depth to admit of the glass containing the nitrogen being turned on one side without air gaining access.

Larger quantities of nitrogen may be obtained in the same way. Other combustibles, as sulphur or a candle, might be used to burn out the oxygen gas from the air, but none answer so quickly and completely as phosphorus, added to which, the products of their combustion would not always be dissolved by water, but would remain mixed with the nitrogen.

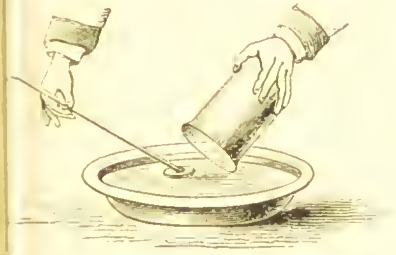


FIG. 8.—Preparation of Nitrogen.

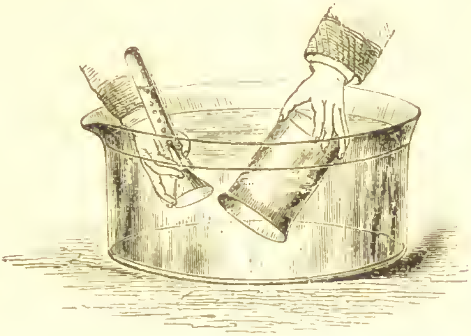


FIG. 9.—Decantation of Gases.

Mem.—The statement concerning the composition of the air is roughly confirmed in isolating nitrogen, about one-fifth of the volume of the air originally in the glass vessel having disappeared, its place being occupied by water.

Properties.—Nitrogen, like oxygen and hydrogen, is colourless, tasteless, and odourless. By pressure, Cailletet and Pictet condensed it to a liquid. Wroblewski and Olszewski obtained it in some quantity as a nearly colourless, transparent fluid, which congeals, by its own evaporation, to a white snow-like solid. It is only slightly soluble in water. *Free* nitrogen is distinguished from most other gases by the absence of any very characteristic or positive properties. Apply a flame to some contained in a tube; it will be found to be incombustible. Immerse a lighted match in the gas; the flame is extinguished, showing that nitrogen is a non-supporter of combustion.

Nitrogen is nearly fourteen times as heavy as hydrogen.

The free nitrogen in the air acts as a diluent of the energetic oxygen, with which it forms merely a *mechanical* mixture.

The air is nearly fourteen and a half (14·44) times as heavy as hydrogen. It may be liquefied and solidified. Its average composition, including minor constituents (which will be referred to subsequently), is as follows:—

Composition of the Atmosphere.

	In 100 volumes.
Oxygen	20·66
Nitrogen	76·95
Argon	·94
Carbonic anhydride	·034
Aqueous vapour	1·40
Ammonia, nitric acid, carburetted hydrogen, hydrogen, ozone, helium, krypton, neon, xenon	traces.
Sulphuretted hydrogen, sulphurous anhydride	traces in towns.

Pure dry air, freed from carbonic anhydride, etc., is remarkably constant in composition, and contains approximately:—

	Per cent. by volume.	Per cent. by weight.
Nitrogen (including argon, etc.)	79·04	76·9
Oxygen	20·96	23·1

Free Nitrogen and Combined Nitrogen.

Notwithstanding the comparative inactivity or negative character of nitrogen in its free condition—that is, when uncombined with other elements—this element, when combined with hydrogen, carbon, oxygen, etc., is a constituent of a large number of important substances, including the ammonium compounds, the various cyanogen compounds, the extensive group of salts called nitrates, the valuable medicinal agents known as alkaloids, the various albumenoid and collagenic matters characteristic of the tissues of animals and plants, and so forth. Free nitrogen is not, however, altogether inactive, for the nitrogen of the air appears to be absorbed and assimilated by some plants—certain crops containing more nitrogen than the soil and manure in which they grew. The absorption is effected by means of nodules which occur on the roots of clover and other leguminous plants; these are the dwelling-places of micro-organisms, and it is through their agency that the soil in which such plants grow becomes richer in nitrogen. Experiments have been made with a view to inducing these organisms to live on the roots of graminaceous plants, for if this could be done a great saving in artificial manures could be effected.

Argon. Krypton. Neon.

It has long been known that when nitrogen is prepared from atmospheric air, the gas obtained is slightly heavier than nitrogen prepared from nitrates or from ammonia. The investigations of Rayleigh and Ramsay have proved that this is due to the presence of another gas, heavier than nitrogen, to which, on account of its apparent chemical inactivity, they gave the name *argon* (*a*, without, *ἔργον*, *ergon*, work). Its density is about 19. It is present in atmospheric air to the extent of nearly 1 per cent. Recently a compound of argon with carbon has been obtained by the passage of electricity between thin carbon poles in an atmosphere of argon; and experiments show that it probably combines with the vapour of magnesium at a very high temperature. Argon and helium occur with nitrogen in the gases of many naturally aërated waters.

Ramsay obtained another element from atmospheric air, to which he gave the name *Krypton* (*κρῦπτος*, *kryptos*, hidden); traces only are present. Ramsay and Travers subsequently announced the presence of another element, *Neon* (*νεος*, *neos*, new), and Ramsay *Xenon*.

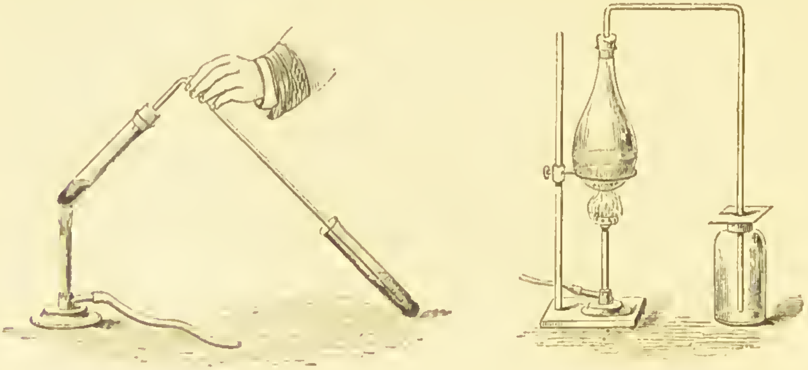
CHLORINE

Source.—The chief source of this element is common salt, more than half of which is chlorine.

Preparation.—About a quarter of an ounce each of salt and of black manganese oxide are mixed, placed in a test-tube, and covered with water; on adding a small quantity of sulphuric acid, evolution of chlorine commences. For the mode of collection see the following paragraphs.

Another process.—As the action of the sulphuric acid on the salt in the above process is mainly to give hydrochloric acid, the latter acid (about 4 parts) and the black manganese oxide (about 1 part) may be used in making chlorine, instead of salt, sulphuric acid, and black manganese oxide.

Collection and Properties.—Free chlorine is a suffocating gas. Care therefore must be observed in experimenting with this element. As soon as its penetrating odour indicates that it is escaping from the test-tube, the cork and delivery-tube (similar to that used in making oxygen) should be fitted on, and the gas led to the bottom of another test-tube containing water (fig. 10). When thirty or forty small bubbles have passed, their evolution being assisted by slightly heating the generating tube, the latter should be removed to the cupboard usually provided in laboratories for performing operations with noxious gases, or be dismounted and the contents carefully and rapidly washed away. The water in the collecting-tube will now be found to smell of the gas, chlorine being soluble in about half its bulk of water. Chlorine water is official in the British Pharmacopœia as "*Solution of Chlorine.*"



Figs. 10 and 11.—Preparation of Chlorine.

Larger quantities may be made from hydrochloric acid and black manganese oxide (4 to 1) in a flask fitted with a delivery-tube, the flask being supported over a flame by the ring of a retort-stand (fig. 11). A piece of cardboard on the neck of the collecting-bottle, as indicated in the figure, retards diffusion of chlorine from the bottle during the process of collection.

Mem.—Flasks and similar glass vessels are less liable to fracture if protected from the direct action of the flame by being placed on a piece of wire gauze about 6 inches square, or on a *sand-bath,* that is, a saucer-shaped tray of sheet iron on which a *thin* layer of sand is placed.

During these manipulations the operator will have noticed that chlorine is of a light yellowish-green colour. The tint is observable when the gas is collected in large vessels. As chlorine is soluble in water ($2\frac{1}{3}$ vols. in 1 vol. at 60° F., 15·5° C.), it cannot be economically stored over that liquid. Being, however, nearly two and a half times as heavy as air, the gas may be collected by simply allowing the delivery-tube to pass to the bottom of a dry test-tube or dry bottle (fig. 11).

An important property of free chlorine is its bleaching-power. Prepare a coloured infusion by placing a few chips of logwood in a test-tube half full of hot water. Pour off some of this red infusion into another tube and add a few drops of chlorine-water; the red colour is rapidly destroyed.

Free chlorine readily decomposes offensive effluvia; it is one of the most powerful of *deodorizers.* It also decomposes putrid and infectious matter; it is one of the best of *disinfectants.* (*Antiseptics* are substances which *prevent* putrefaction.)

Combination of Hydrogen with Chlorine, forming Hydrochloric Acid.—If an opportunity occurs of generating chlorine in a closed chamber or in the open air, a test-tube, of the same size as one of those in which hydrogen has been retained from a previous operation, is filled with the gas. The hydrogen-tube is then inverted over that containing the chlorine, the mouths being kept together by encircling them with a finger. After the gases have mixed, the mouths of the tubes are quickly brought into contact with a flame, when explosion occurs and fumes of a compound of hydrochloric acid gas with the moisture of the air are formed. The Hydrochloric Acid of pharmacy (*Acidum Hydrochloricum*, B.P.) is a solution of this gas (made in a more economical way) in water.

The foregoing experiment affords evidence of the powerful affinity of chlorine and hydrogen for each other. Chlorine dissolved in water will, in sunlight, slowly remove hydrogen from some of the water and liberate oxygen. The bleaching-power of chlorine is generally referred to this indirect oxidizing effect which it produces in presence of water; for dry chlorine does not bleach.

Density.—Chlorine is more than 35 times as heavy as hydrogen. A wine-bottle would hold about 35 grains.

SULPHUR, CARBON, IODINE

The physical properties (colour, hardness, weight, etc.) possessed by these elements, when they are in the free state, are probably familiar to the student. Some of their leading chemical characters will also be understood when a few facts concerning each are made the subject of experiment.

Sulphur.—Burn a small piece of sulphur; a penetrating odour is produced, due to the formation of a colourless gas. This product is a chemical compound formed by the union of the oxygen of the air with the sulphur. It is termed sulphurous anhydride (or sulphurous acid gas).

Carbon in a more or less pure condition, is familiar, in the free form, as soot, coke, charcoal, graphite (or plumbago, popularly termed blacklead), and diamond. The presence of combined carbon, in wood and in other vegetable and animal matter, is at once rendered evident by heat. Place a little tartaric acid on the end of a knife in a flame; the blackening that occurs is due to the separation of carbon. The black matter at the extremity of a piece of half-burned wood also is free carbon.

Carbon, like hydrogen, phosphorus, and sulphur, has a great affinity for oxygen at high temperatures. A striking evidence of that affinity is the evolution, during its combustion, of sufficient heat to make the materials concerned red- or even white-hot. When ignited in the diluted oxygen of the air, carbon simply burns with a moderate glow, as seen in an ordinary coke or charcoal fire; but when ignited in pure oxygen, the intensity of its combustion is greatly exalted. The product of the combination of the two elements, if the oxygen be in excess, is an invisible gas termed carbonic anhydride (or carbonic acid gas); if the carbon be in excess and the temperature very high, another invisible gas, termed carbonic oxide, results.

Iodine.—A prominent chemical characteristic of free iodine is its great affinity for metals. Place a piece of iodine, about the size of a pea, in a test-tube with a small quantity of water and add a few iron filings or small nails. On gently warming this *mechanical* mixture, or even shaking, if longer time be allowed, the colour and odour of the iodine disappear; it has *chemically* combined with the iron—a *chemical compound* has been produced. If the liquid be filtered, a clear aqueous solution of the compound of the two elements is obtained.

This compound is an iodide of iron. Its solution, made as above, and mixed with sugar, forms, when of a certain strength, the ordinary Syrup of Ferrous Iodide of pharmacy (*Syrupus Ferri Iodidi*, B.P.). The solid iodide is obtained on removing the water of the above solution by evaporation.

Sulphur and *Iron*, also, when very strongly heated, *chemically combine* to form a substance which has none of the properties of a *mixture* of sulphur and iron—that is, has none of the characters of sulphur and none of iron, but new properties altogether. The product is termed Ferrous Sulphide. Its manufacture and uses will be alluded to in treating of the compounds of iron; it is mentioned here as a simple but striking illustration of the difference between a *chemical compound* and a *mechanical mixture*.

THE ELEMENTS

From the foregoing statements a general idea will have been obtained of the nature of several of the more frequently occurring elements. Some additional facts concerning them may be gathered from the following Table, which gives the origin of the names of a number of the elements :—

Aluminium . .	The metallic basis of alum was at first confounded with that of iron sulphate, which was the alum of the Romans, and was so called in allusion to its tonic properties, from *alo*, *I nourish*.
Ammonium .	This body is not an element ; but its components exist in all ammoniacal salts, and apparently play the part of such elements as potassium and sodium. Sal ammoniac (ammonium chloride) was first obtained from near the temple of Jupiter Ammon in Libya ; hence the name.
Antimony . . . **(Stibium)**	Στίβι (stibi), or στίμμι (stimmi), was the Greek name for the native antimony sulphide. The word *antimony* is said to be derived from ἀντὶ (anti) *against*, and *moine*, French for *monk*, from the fact that certain monks were poisoned by it.
Argon	From α, without ; ἔργον (ergon), work.
Arsenium, Arsenicum, or Arsenic	Ἀρσενικὸν (arsenikon), the Greek name for orpiment, an arsenium sulphide. Common *white arsenic* is arsenium oxide.
Barium . . .	From βαρὺς (barūs) *heavy*, in allusion to the high specific gravity of "heavy spar," the most common of the barium minerals.
Bismuth . . .	Slightly altered from the German *Wismuth*, derived from *Wiesematte*, "a beautiful meadow," a name given to it originally by the old miners in allusion to the prettily variegated tints presented by the freshly exposed surface of this crystalline metal.
Boron	From *borak* or *baurak*, the Arabic name of *borax*, the substance from which the element was first obtained.
Bromine . . .	From βρῶμος (brōmos), a *stink*. It has an intolerable odour.
Cadmium . . .	Καδμεία (kadmeia) was the ancient name of calamine (zinc carbonate), with which cadmium carbonate was long confounded, the two often occurring together.
Calcium . . .	*Calx*, *lime*, calcium oxide.
Carbon . . .	From *carbo*, *coal*, which is chiefly carbon.
Cerium. . .	Discovered in 1803, and named after the planet *Ceres*, which was discovered on Jan. 1, 1801.

Chlorine . . .	From χλωρὸς (chlōros) *green*, the colour of this element.
Chromium . .	From χρῶμα (chrōma) *colour*, in allusion to the characteristic appearance of its salts.
Cobalt	*Cobalus*, or *Kobold*, was the name of a demon supposed to inhabit the mines of Germany. The ores of cobalt were formerly troublesome to the German miners, and hence received the name their metallic radical now bears.
Copper (Cuprum)	From *Cyprus*, the name of the Mediterranean island where this metal was first worked.
Fluorine . . .	From *fluo*, *I flow*. Calcium fluoride, its source, is commonly used as a flux in metallurgic operations.
Gold (Aurum) .	*Aurum* (Latin) from a Hebrew word signifying the colour of fire. *Gold*; a similar word is expressive of *bright yellow* in several old languages.
Hydrogen . . .	From ὕδωρ (hudōr) *water*, and γένεσις (genesis), *generation*, in allusion to the product of its combustion in air.
Iodine	From ἴον (ion) *a violet*, and εἶδος (eidos) *likeness*, in reference to the colour of its vapour.
Iron (Ferrum) .	Prehistoric. The spelling may be from the Saxon *iren*, the pronunciation from the Gothic "*iarn*." The derivation is perhaps Aryan; it probably originally meant *metal*.
Lead (Plumbum)	The Latin expresses "something heavy"; the Saxon *lad* has a similar signification.
Lithium . . .	From λίθειος (litheios) *stony*, in allusion to its supposed existence in the mineral kingdom only.
Magnesium . .	From *Magnesia*, the name of the town (in Asia Minor) near which the substance now called "native magnesium carbonate" was first discovered.
Manganese . .	Probably the slightly altered word *magnesia*, with whose compounds those of manganese were confounded till 1740.
Mercury . . . **(Hydrargyrum)**	*Hydrargyrum*, from ὕδωρ (hudōr) *water*, and ἄργυρος (arguros) *silver*, in allusion to its liquid and lustrous characters. *Mercury*, after the messenger of the gods, on account of its susceptibility of motion. The old name *quicksilver* also indicates its ready mobility and silvery appearance.
Nickel	*Nickel*, from *nil*, *worthless*. Nickel ore was formerly called *Kupfernickel*, *false copper*. When a new element was found in the ore, the name nickel was retained for it.
Nitrogen . . .	From νίτρον (nitron) and γένεσις (genesis) *generation*, *i.e.*, *generator of nitre*.

Oxygen . . .	From ὀξὺς (oxūs) *acid*, and γένεσις (genesis) *generation*, *i.e.*, generator of acids. When first discovered it was supposed to enter into the composition of all acids.
Phosphorus . .	Φῶς (phōs) *light*, and φέρειν (pherein) *to bear*. The light it emits may be seen on exposing it in a dark room.
Platinum . . .	From *platina* (Spanish), diminutive of *plata*, *silver*. It somewhat resembles silver, but is less white and lustrous.
Potassium . . . **(Kalium)**	*Kalium* from *kali*, Arabic for *ashes* (see Sodium). Manufactories in which compounds of potassium and allied sodium salts are made, are called *alkali*-works to this day. *Potassium*, from *potash*. Potash so called because obtained by evaporating the lixivium of wood-ashes in pots.
Silicon	From *silex*, Latin for *flint*, which is nearly all silica (silicon oxide).
Silver . . . . **(Argentum)**	Ἄργυρος (arguros) *silver*, from ἀργὸς (argos) *white*. Words resembling the term *silver* occur in several languages, and indicate a white appearance.
Sodium (Natrium)	*Natrium*, from *natron*, the old name for certain natural deposits of sodium carbonate. *Sodium*, from *soda*, the name originally given to the residue of the combustion of marine plants. Soda ashes were chemically distinguished from pot-ashes by Duhamel in 1736. Previously both were simply *kali* or *ashes* from two different sources. Sir Humphry Davy first isolated the two metals, in 1807.
Strontium . . .	This name is commemorative of *Strontian*, a mining-village in Argyleshire, Scotland, in the neighbourhood of which the mineral known as *strontianite*, or strontium carbonate, was first found.
Sulphur . . .	From *sal*, a *salt*, and πῦρ (pūr) *fire*, indicating its combustible qualities. Its common name, *brimstone*, has the same meaning, being the slightly altered Saxon word, *brynstone*, *i.e.*, burnstone.
Tin (Stannum) .	Both words are possibly corruptions of the old British word *staen*, or the Saxon word *stan*, a stone. Tin was first discovered in Cornwall, and the ore (an oxide) is called *tinstone* to the present day.
Zinc	From Ger. *Zinn*, *tin*, with which Zinc seems at first to have been confounded.

QUESTIONS AND EXERCISES

Distinguish between the *art* and the *science* of chemistry.—Of how many elements is terrestrial matter composed?—Enumerate the chief non-metallic elements.—Describe a process for the preparation of oxygen.—How are gases usually stored?—Mention the chief properties of oxygen.—What is the source of animal warmth?—State the proportion of oxygen in air.—Is the proportion constant, and why?—Give a method for the elimination of hydrogen from water.—State the properties of hydrogen.—Why is a mixture of hydrogen and air explosive?—Explain the effects producible by the ignition of large quantities of coal-gas and air.—What is the nature of combustion?—Define a *combustible* and a *supporter of combustion*.—Describe the structure of flame.—State the principle of the Davy safety-lamp.—In what proportion is hydrogen lighter than oxygen?—What do you mean by *diffusion* of gases?—State Graham's law concerning diffusion.—Name the source of phosphorus, and give its characters.—Why does phosphorus burn in air?—What gas remains when ignited phosphorus has removed all the oxygen from a confined portion of air?—Mention the properties of nitrogen.—What office is fulfilled by the nitrogen of the air?—State the proportions of the chief constituents of air?—Mention the minor or occasional constituents of air.—What is the proportion by weight of nitrogen to oxygen in the atmosphere?—Give the specific gravity of nitrogen.—How is chlorine prepared?—Enumerate the properties of chlorine.—Define the terms *deodorizer* and *disinfectant*.—Explain the bleaching effect of chlorine.—What proportion of hydrogen to chlorine is necessary for the formation of hydrochloric acid gas?—State the prominent chemical and physical characters of sulphur.—State those of carbon.—State those of iodine.—Give the derivations of the names of some of the elements.

NUMERICAL AND PHYSICAL MATTERS OF SPECIAL IMPORTANCE IN ELEMENTARY CHEMISTRY

The Metric System of Weights and Measures (the word *metric* is from the Greek *μέτρον, metron,* measure) which is now in common use in most of the countries of Europe and elsewhere, presents several advantages over the British Imperial system. The two chief advantages of the metric system are, that certain of the units are related to one another in an exceedingly simple and practical manner; and that the system is a decimal one throughout, and is thus in complete harmony with the universal mode of counting.

The system of weights and measures legalised by the Weights and Measures (Metric System) Act, 1897, for employment in this country for all purposes, is founded on the metre. Fig. 12 represents a pocket folding measure the tenth part of a metre in length, divided into 10 centimetres, and each centimetre into 10 millimetres.

The units of the system, with their multiples and submultiples, are as follows:—

Length.—The *Unit of Length* is the Metre, derived from the measurement of the Quadrant of a Meridian of the Earth. (Practically it is the length of certain carefully preserved bars of metal, from which copies have been taken.)

Surface.—The *Unit of Surface* is the Are, which is the square of Ten Metres.

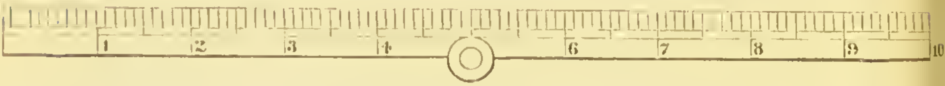


Fig. 12. The Decimetre.

Cubic Measure.—The *Unit of Cubic Measure* is the Cubic Decimetre, which is the Cube of the Tenth part of a Metre.

Capacity.—The *Unit of Capacity* is the Litre. It was originally intended that the Litre should be exactly one Cubic Decimetre, but the Standard Litre although very nearly in conformity with this intention is not absolutely so. (1 Litre = 1.00016 Cubic Decimetre.)

As defined in the Schedule to an Order in Council of 19th May 1898:—

> "The Litre is represented by the capacity at 0° Centigrade of the cylindrical brass measure marked 'Litre, 1897' (which is deposited with the Board of Trade), and having a diameter equal to one-half its height. This Litre at 0° Centigrade when full contains one Kilogram of distilled water at the temperature of 4° Centigrade, under an atmospheric pressure equal to that represented by a column of mercury 760 Millimetres high at 0° Centigrade, at sea level, and at latitude 45°; the weighing being made in air, but reduced by calculation to a vacuum. It is the only unit of metric measure of capacity from which all other metric measures of capacity, as well for liquids as for dry goods, shall be ascertained."

Mass.—The *Unit of Mass* is the Gramme,* which is the mass of that quantity of distilled water, at its maximum density point (4° C.) which occupies the space of the one-thousandth part of a Litre (1 Millilitre).

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* The word *gramme* is sometimes, unfortunately, written *gram*, which for use in Britain, India, and the Colonies, too closely resembles the word *grain*.

Table.

Note.—Multiples are denoted by the Greek words "Deka," Ten, "Hecto," Hundred, "Kilo," Thousand.
Subdivisions by the Latin words, "Deci," One-tenth, "Centi," One-hundredth, "Milli," One-thousandth.

uantities.	Length.	Surface.	Capacity.	Weight.
000	Kilo-metre	...	Kilo-litre	Kilo-gramme
100	Hecto-metre	Hectare	Hecto-litre	Hecto-gramme
10	Deca-metre	...	Deca-litre	Deca-gramme
1 (Units)	**METRE**	**ARE**	**LITRE**	**GRAMME**
·1	Deci-metre	...	Deci-litre	Deci-gramme
·01	Centi-metre	Centiare	Centi-litre	Centi-gramme
·001	Milli-metre	...	Milli-litre	Milli-gramme

When the Metric method is exclusively adopted in Great Britain, these Units and Table, comprising the entire System f Weights and Measures, represent all that will be essential to be learnt in lieu of the numerous and complicated Tables hitherto in use. Adopting the style of elementary books on rithmetic, the table may be expanded thus:—

10 milligrammes make 1 centigramme; 10 centigrammes make 1 decigramme; 10 decigrammes make 1 gramme; 10 grammes make 1 decagramme, or dekagramme; 10 decagrammes make 1 hectogramme; 10 hectogrammes make 1 kilogramme; 10 millilitres make 1 centilitre, etc.; 10 millimetres make 1 centimetre, etc.

Abbreviations.—Metre = *m*; decimetre = *dm*; centimetre = *m*; millimetre = *mm*; kilometre = *km*. Square metre = m^2; ubic metre = m^3; and so on. Litre = *l*; decilitre *dl*, etc. Kilogramme = *kg*; dekagramme = *dkg*; gramme = *g*; decigramme = *dg*; centigramme = *cg*; and milligramme = *mg*.

The following approximate British equivalents of metrical units should be committed to memory:—

1 Metre = 3 feet 3 inches and 3 eighths.
1 Are = a square whose side is 11 yards.
1 Litre = 1¾ pint.
1 Gramme = 15½ grains.
The Kilometre is equal to 1100 yards.
The Hectare = 2½ acres nearly.
The Metric Ton of 1000 Kilogrammes = 19 cwt. 2 qrs. 20 lbs. 10 oz.
The Kilogramme = 2 lbs. 3¼ oz. nearly.

A litre of water at 39° F. (3·9° C.) weighs 15,432 grains; at 50° F. (10° C.), 15,429 grains; at 60° F. (15·5° C.), it weighs 15,418 grains; at 70° F. (21·1° C.), 15,403 grains; and at 80° F. (26·7° C.), 15,383 grains (Pile).

Decimal Coinage.—In most countries where the metric system of weights and measures is employed, a decimal coinage is also adopted. This, conjoined with the ordinary decimal method of enumerating, which fortunately is in universal use, simplifies calculations of all kinds.

The General Council, under whose authority the British Pharmacopœia is issued, encourages medical practitioners and pharmacists in the adoption of the metric system, and gives the annexed statement of metric weights and measures.

WEIGHTS AND MEASURES OF THE METRIC SYSTEM

WEIGHTS.

1 Milligramme = the thousandth part of one grm. or 0·001 grm.
1 Centigramme = the hundredth ,, 0·01 ,,
1 Decigramme = the tenth ,, 0·1 ,,
1 Gramme = weight of one millimetre of distilled water at 4° C. (39·2° F.)
1 Dekagramme = ten grammes 10·0 ,,
1 Hectogramme = one hundred grammes 100·0 ,,
1 Kilogramme = one thousand grammes 1000·0 (1 kilo.).

MEASURES OF CAPACITY.

1 Millilitre = the volume at 4° C. of 1 gramme of water.
1 Centilitre = ,, ,, 10 ,, ,,
1 Decilitre = ,, ,, 100 ,, ,,
1 Litre = ,, ,, 1000 ,, (1 kilog.).

MEASURES OF LENGTH.

1 Millimetre = the thousandth part of one metre or 0·001 metre.
1 Centimetre = the hundredth ,, ,, 0·01 ,,
1 Decimetre = the tenth ,, ,, 0·1 ,,
1 Metre = 1·0 ,,

WEIGHTS AND MEASURES OF THE IMPERIAL SYSTEM

WEIGHTS.

1 Grain gr.
1 Ounce oz. = 437·5 grains.
1 Pound lb. = 16 ounces = 7000·0 ,,

MEASURES OF CAPACITY.

1 Minim	min.		
1 Fluid Drachm	fl. drm.	=	60 minims.
1 Fluid Ounce	fl. oz.	=	8 fluid drachms.
1 Pint	O.	=	20 fluid ounces.
1 Gallon	C.	=	8 pints.

MEASURES OF LENGTH.

1 Inch	in.		
1 Foot	ft.	=	12 inches.
1 Yard	yd.	=	36 ,,

RELATION OF VOLUME TO MASS.

1 Minim is the volume at 62° F. of			0·9114583 grain of water.		
1 Fluid Drachm	,,		54·6875 grains of water.		
1 Fluid Ounce	,,	1 ounce, or	437·5	,,	,,
1 Pint	,,	1·25 pounds, or	8750·0	,,	,,
1 Gallon	,,	10 pounds, or	70000·0	,,	,,
109·7143 minims = the volume at 62° F. of 100				,,	,,

QUESTIONS AND EXERCISES

Mention some advantages of the metric (decimal) system of weights and measures.—What is the chief unit of the metric system?—Mention the names of the metric units of surface, capacity, and mass, and state how they are derived from the unit of length.—How are multiples of metric units indicated?—State the designations of submultiples of metric units.—How many metres are there in a kilometre?—How many millimetres in a metre?—How many grammes in 5 kilogrammes?—How many milligrammes in 13½ grammes?—In 1898 centigrammes how many grammes?—In a metre measure 5 centimetres wide and 1 centimetre thick, how many cubic centimetres?—How many litres are contained in a cubic metre of any liquid?—State the British equivalent of the metre.—How many square yards in an are?—How many fluid ounces in a litre?—How many ounces in a kilogramme?—Give the relation of a metric ton (1000 kilos.) to a British ton.—How many grains are there in 1 British ton?—How many ounces in 1 ton?—How many grains of water in 1 fluid drachm?—How many minims in 1 pint?—How many grains in 1 pint of water?

Measurement of Temperature. Fahrenheit and Centigrade Thermometer Scales (fig. 13).—The measurement of temperature is carried out by aid of the *thermometer*,* the construction of which is described in the Section on Quantitative Measurements. The thermometers employed in Britain are practically always graduated in accordance with either the Fahrenheit or the Centigrade scale. On the Centigrade (C.) scale the freezing-point of water is marked zero, and the boiling-point 100; on the Fahrenheit (F.) scale the zero is placed 32 degrees below the freezing-point of water, and the boiling-point is 212. Conversions of expressions of temperatures in degrees F. into the corresponding expressions in degrees C., and conversions in the reverse direction, can be made by applying the following rules:—

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* From *θέρμη*, *therme*, heat, and *μέτρον*, *metron*, measure.

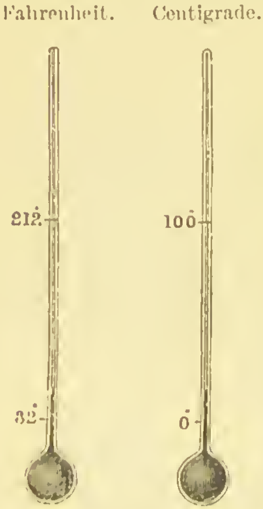

Fig. 13.
Thermometric Scales.

1. F. to C. Subtract 32, multiply the remainder by 5, divide the product by 9.

Example:—68° F. Find the corresponding ° C.

$68 - 32 = 36$; $36 \times 5 = 180$; $180 \div 9 = 20$.

68° F. corresponds to 20° C.

2. C. to F. Multiply by 9, divide the product by 5, add 32.

Example:—52° C. Find the corresponding ° F.

$52 \times 9 = 468$; $468 \div 5 = 93{\cdot}6$; $93{\cdot}6 + 32 = 125{\cdot}6$.

52° C. corresponds to 125·6° F.

The following is an easily remembered rule for converting from ° C. to ° F.:—

Double the number of degrees C., subtract from the result its tenth part, add 32.

Thus, applying the rule to the example immediately preceding:

$52 \times 2 = 104$; $104 - 10{\cdot}4 = 93{\cdot}6$; $93{\cdot}6 + 32 = 125{\cdot}6$.

52° C. corresponds, as above, to 125·6° F.

Care must be taken in dealing with expressions of temperature having the − sign; that is, with expressions representing temperatures below the zero points of the respective scales.

Example:—−4° F. Find the corresponding ° C.

$-4 - 32 = -36$; $-36 \times 5 = -180$; $-180 \div 9 = -20$.

−4° F. corresponds to −20° C.

Measurement of Atmospheric Pressure. The Barometer.—The analysis of gases and vapours involves determinations of the varying pressure of the atmosphere as indicated by the *barometer* (from βάρος, *baros,* weight, and μέτρον, *metron,* measure).

The ordinary mercurial barometer is a glass tube 33 or 34 inches long, closed at one end, which has been filled with mercury and inverted in a small cistern or cup of mercury (fig. 14). The greater part of the mercury remains in the tube, owing to the pressure of the atmosphere on the exposed surface of the liquid, the average height of the column being nearly 30 inches. In the popular form of the instrument, the wheel barometer, the cistern is formed by a recurvature of the tube (fig. 15); on the exposed surface of the mercury a float is placed, from which a thread passes over a pulley and moves an index whenever the column of mercury rises or falls. The glass tube and contained column of mercury are altogether enclosed, the index alone being visible. In the form first described the upper end of the glass tube and mercurial column are exposed, and the height of the mercury is ascertained by direct observation.

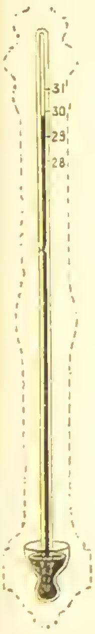

Fig. 14.
Barometer.

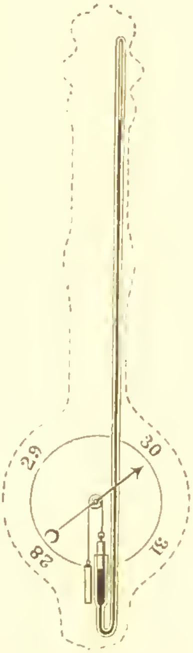

Fig. 15.
Barometer.

The aneroid barometer (from ἀ, *a,* without, and νηρὸς, *nēros,* fluid) consists of a small, shallow, vacuous metal drum, the sides of which approach each other when an increase of atmospheric pressure occurs, their elasticity enabling them to recede towards their former position on a decrease of pressure. This motion is so multiplied and altered in direction by levers, etc., as to act on a hand traversing a plate on which are marked numbers corresponding with those showing the height of the mercurial column of the ordinary barometer by which the aneroid was adjusted. *The Bourdon barometer* (from the name of the inventor) is a modified aneroid, containing in the place of the round metal box a flattened vacuous tube of metal bent nearly to a circle. These barometers are also used for measuring the pressure in steam-boilers, etc. Under the name of *pressure-gauges* they are sold to indicate pressures of as much as 500 pounds per square inch or higher. Aneroid barometers, on account of their portability (they can be made of 1 to 2 inches in diameter and less than an inch thick), are handy companions for ascertaining the heights of hills, mountains, and other elevations.

QUESTIONS AND EXERCISES

Give rules for the conversion of degrees C. into degrees F., and of degrees F. into degrees C.—Name the degree C. equivalent to 60° F. —What degree C. is represented by –4° F.?—Mention the degree F. indicated by 20° C.—Convert 100° F. into degrees C.—How are variations in atmospheric pressure determined?—Explain the construction and mode of action of barometers.—In what respect does a wheel-barometer differ from an instrument in which the readings are taken from the top of the column of mercury?—Describe the construction and mode of action of an aneroid barometer.

Relation of the Volume of a Gas to Pressure and to Temperature.

The volume occupied by any given quantity of a gas varies (*a*) with variations in the pressure to which it is subjected; and (*b*) with variations in its temperature. The amount of the variation in volume for any given change in either of these conditions is practically independent of the nature of the gas, since (within moderate ranges of pressure and of temperature) it is approximately the same for all gases, unless these are near their liquefying points. The observed variations take place approximately in accordance with the following laws:—

Boyle's Law.—When the temperature of a quantity of gas is kept constant, the volume which the gas occupies varies *inversely* as the pressure. When the original pressure is doubled, the volume is diminished to one-half; when it is trebled, the volume is diminished to one-third; when it is halved, the volume is doubled, and so on. The pressure under which a gas is measured is expressed in millimetres of mercury—that is, by the height in millimetres of a column of mercury capable of counter-balancing the pressure exerted by the gas.

Charles's Law.*—When the pressure under which a quantity of gas is measured is kept constant, the volume which the gas occupies varies *directly* as the "absolute" temperature. The absolute temperature is obtained by adding 273 to the observed temperature of the gas in degrees Centigrade. Suppose that a quantity of gas occupies 273 c.c. at 0° C., then the volumes which it is found to occupy at the temperatures in Column I. of the following table are those given in Column III. Columns II. and III. show how the volume varies directly as the absolute temperature.

I. Temperature in ° C. (=t.).	II. Absolute Temperature (=273+t.).	III. Volume in c.c.
1	274	274
2	275	275
10	283	283
30	303	303
−1	272	272
−10	263	263
−30	243	243

This table illustrates another way in which Charles's law may be stated, viz., that the volume of a gas is increased or diminished by $\frac{1}{273}$ (=0·00366) of its volume at 0° C. for each degree Centigrade that the temperature of the gas is raised or lowered.

Standard Temperature and Pressure.—The temperature of 0° C. and the pressure of 760 mm. are termed *standard temperature* and *standard pressure* respectively.

It is frequently necessary to calculate, in accordance with the foregoing laws, what the volume of a quantity of gas would become under new conditions of pressure and of temperature, when its volume under stated conditions (original conditions) is known. The calculation (which is often termed "correction for pressure and temperature") can be made in all such cases in accordance with the following fairly obvious rule:—

Taking the known volume,

(1) Multiply by the original pressure, and divide by the new pressure; and

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* Also occasionally called "Gay Lussac's Law."

(2) Multiply by the new absolute temperature, and divide by the original absolute temperature.

Example:—A quantity of hydrogen occupies 260 c.c. at 27° C. and 750 mm. Find its volume at 0° C. and 780 mm.

We have here:—Known volume = 260 c.c.; Original Pressure = 750 mm.; New Pressure = 780 mm.; Original Absolute Temperature = $273 + 27° = 300°$; New Absolute Temperature = $273 + 0° = 273°$.

Proceeding as indicated by the rule given above, we get:

$$260 \times \frac{750}{780} \times \frac{273}{300} = 227{\cdot}5 \text{ c.c.*}$$

Density.—By the density of a substance we understand the number of units of mass of the substance which occupy a unit of space. The gramme and the millilitre are adopted as unit of mass and unit of space respectively, and the density of a substance is then represented by the number of grammes of that substance which occupy a millilitre. At 4° Centigrade one gramme of water occupies a millilitre, hence at this temperature the density of water is = 1 in terms of the above units.

Relative Densities (or Specific Gravities) of Liquids and of Solids.—Relative densities (or specific gravities) are the densities of other substances as compared with that of some substance which is chosen as standard. Water at 4° C. (with density assumed = 1) would be a theoretically perfect standard for the comparison of the relative densities of other liquids and of solids. At 4° Centigrade water is at its *maximum density point;* that is to say, any given quantity of water occupies at this temperature a smaller volume than it does at any temperature above or below 4° C. The numbers representing the relative densities of solids and of liquids, in terms of the units and standard referred to above,† would thus show how many times heavier or lighter the respective substances are, bulk for bulk, than water at 4° C.; or, what is the same thing, how many grammes of the respective substances occupy the same space as one gramme of water at 4° C. (*i.e.* 1 millilitre).

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* For more detail than can be given here, and for numerous examples, see *Arithmetical Exercises in Chemistry*, by Leonard Dobbin, Ph.D. [Edinburgh: James Thin.]

† Note, however, that the standard temperature adopted in practice for comparing specific gravities is not 4° C., but 15·5° C. (60° F.). (*See* the Section on Quantitative Measurements.)

Relative Densities of Gases.—The relative densities (or specific gravities) of other gases are usually compared with the density of hydrogen, the lightest known gas, which is arbitrarily chosen as standard, with density = 1. (Formerly air was the standard adopted, with density = 1.) In order to be in a position to compare the density of any given gas with that of the standard, it is necessary to determine the masses of equal volumes of both gases, under the same conditions of pressure and of temperature (*see* p. 36, and the Section on Quantitative Measurements). The numbers representing the relative densities of gases show how many times heavier the respective gases are, bulk for bulk, than hydrogen under the same conditions of pressure and of temperature, or, what is the same thing, how many grammes of the respective gases occupy, under the same conditions of pressure and of temperature, the same space as one gramme of hydrogen (*i.e.* 11·1 litres).

Vapour Density.—This term is applied to the relative density (or specific gravity) of the vapour in the case of any substance which is liquid or solid at ordinary temperatures but which is capable of being converted into the state of vapour, without undergoing decomposition, by a sufficient rise of temperature. Vapour densities are thus strictly comparable with the relative densities of gases. (*See* the Section on Quantitative Measurements.)

QUESTIONS AND EXERCISES

Define Boyle's law.—What does the volume of a litre of hydrogen at ordinary atmospheric pressure become when the pressure is doubled, halved, quadrupled?—Mention two ways in which the regularity known as Charles's law may be stated.—How is the number which represents the absolute temperature obtained?—Define standard temperature and pressure.—What is the rule for "correcting" the volume of a gas for change in temperature and pressure?—What do you understand by the terms density, relative density, vapour density?

The student is recommended to read the following paragraphs on the General Principles of Chemical Philosophy carefully once or twice, then to study (experimentally, if possible) the succeeding pages, returning to and reading over the General Principles from time to time until they are thoroughly comprehended.

THE GENERAL PRINCIPLES OF CHEMICAL PHILOSOPHY

The Science of Chemistry treats of a particular class of changes that matter undergoes. These changes result in the formation of new substances—that is, of substances which are different in composition and properties from the materials out of which they have been produced—and they are commonly called *chemical changes*. Such changes may be the result of natural agencies only, as in the growth of plants and animals in a wholly natural state, and in the transformations that the inanimate materials of which the earth is composed undergo owing to climatic and other influences; or they may be directed and, so far, controlled by human agency, as, for example, in the processes carried out in the chemical laboratory or manufactory.

Chemical and Physical Changes.—Many well-marked, or *typical*, cases of chemical change are easily recognised as such. Sometimes, however, it is difficult, and occasionally it is not possible, to recognise whether a particular change really is a chemical change, or whether it belongs to the class of phenomena called physical changes. The existence of any uncertainty arises from the difficulty in proving conclusively whether a new substance has been produced or not, together with the fact that it is not an altogether easy matter to define strictly what constitutes the formation of a new substance. Familiar examples of physical changes are furnished by the transformations of solids into the liquid state (as of ice into water) or of liquids into the state of vapour (as of water into steam) without any change in the composition of the substances. In typical cases, the occurrence of chemical change may usually be recognised by the accompanying phenomena characteristic of such change. Two of the most important of these phenomena are:—

1. *The disappearance of the properties of the substance or substances which take part in the change, and the formation of a new substance or of new substances possessing other properties.*

A *mixture* of free oxygen and hydrogen is still a gas; water, *a chemical compound* of oxygen and hydrogen, is a liquid; here is great alteration in properties. Iodine is only slightly soluble in water, forming a brown-coloured solution, and iron is insoluble; but when iodine and iron are *chemically* combined, the product is very soluble in water, forming a light-green solution which is utterly unlike iron or iodine in any one of its properties, and in which the eye can detect neither iodine nor iron. Tartaric acid and sodium carbonate, mixed together in presence of water, give rise to other and wholly different *chemical compounds*, the original substances having interacted and formed fresh combinations. Sand, sugar, and butter, rubbed together, form *a mere mixture*, from which water would extract the sugar, and ether dissolve out the butter, leaving the sand. These examples illustrate how *chemical* action is distinguished, namely, by producing an entire change of properties in the resulting substances.

2. *The giving out, or the absorption of heat, during the change.* When coal or a candle burns in the air, the carbon present in the combustible material unites with the oxygen of the atmosphere, with the evolution or giving out of heat. Sulphur, phosphorus, certain metals such as magnesium and zinc, as well as many other substances, likewise burn in the air, with the evolution of heat. These instances of combustion are all examples of chemical action, and are readily distinguishable as such.

Besides the two important phenomena noted above as characteristic of chemical changes, it is further to be observed that chemical combination takes place between the substances which enter into reaction (interact) in certain definite proportions by weight only, and not simply in any proportions in which they may, by chance or by intention, be mixed together. The quite general regularities that have been observed in connection with this matter are discussed below under the Laws of Chemical Combination.

Elements and Compounds.—In modern chemistry the term *element* is applied to any substance which has not been shown to be compound—that is, to possess a composite nature. The word is strictly reserved for those substances which the chemist is neither able to break up into two or more simpler substances, nor to produce by the union of two or more simpler substances. The elements are the simplest forms of matter known. The term *compound* is applied to all substances the composite nature of which can be proved. The proof may consist in breaking up the compound into two or more simpler substances by some method of *decomposition*; or it may consist in building up the compound from two or more simpler substances, by causing these to combine—that is, by effecting its *synthesis*.*

Up to the present, about 70 elements have been discovered, and more or less minutely examined and described. Of these elements, about 40 are either of practical importance themselves, or they enter into the composition of compounds which are of practical importance. All of the enormous number of chemical compounds that have been prepared and examined are combinations of two or more of the known elements.

Chemical Affinity is the name applied to that tendency exhibited by certain elementary and compound substances to enter into fresh combinations with one another so as to form new compounds. The name is sometimes applied also to the tendency of substances to remain combined after combination, with the formation of new compounds, has taken place.

Laws of Chemical Combination.—Chemical combination takes place between definite quantities of substances. The more important quantitative relations are expressed by the following laws:—

The Law of Constant Proportions states that the same chemical compound is always composed of the same elements, and that these elements are present in the compound in the same relative proportions by weight. Thus any pure specimen of common salt is found on analysis to contain the elements sodium and chlorine only, and these are associated with each other in the proportions of 23 parts by weight of sodium to 35·4 parts by weight of chlorine. Similarly any pure specimen of sulphuric acid contains hydrogen, sulphur, and oxygen, associated with one another in the proportions of 2 parts by weight of hydrogen to 31·82 of sulphur and 63·52 of oxygen. To the general statement of the law of constant proportions, it may be added that the mass of (or quantity of matter contained in) any compound substance is equal to the sum of the masses of its constituents.

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* The word *synthesis* is from σύνθεσις, *sunthesis*, a putting together; *analysis*, a term often used to designate the reverse operation of decomposition, is from ἀναλύω, *analuō*, I resolve

The Law of Multiple Proportions.—The same elements are sometimes capable of uniting with each other in more than one proportion by weight. The law of multiple proportions states that, when this is the case, the several quantities of one of the elements which combine to form two or more compounds with any given quantity of the other element, stand in simple multiple relations either to each other or to some common submultiple. Thus in the two oxides of carbon there are contained :

	Parts by weight of Carbon.	Parts by weight of Oxygen.
Carbonic oxide . . .	12	16
Carbonic anhydride . .	12	32

and in the two oxides of phosphorus there are contained :

	Parts by weight of Phosphorus.	Parts by weight of Oxygen.
Phosphorous anhydride . .	62	48 (= 16 × 3)
Phosphoric anhydride . .	62	80 (= 16 × 5)

The Law of Gaseous Volumes states that when gases combine with one another, the volumes which unite stand in a simple relation to each other and also to the volume of the product when this is a gaseous substance. The simple relations of the volumes of the combining gases to each other and to the volume of the product in a few cases illustrative of this law, are exhibited in the following table :—

Volumes of combining gases.	Volume of product.
Hydrogen 1, Chlorine 1	Hydrochloric acid 2
Hydrogen 2, Oxygen 1	Water vapour 2
Carbonic oxide 2, Oxygen 1	Carbonic anhydride 2
Carbonic oxide 1, Chlorine 1	Phosgen 1

N.B.—In each of the foregoing cases it is necessary to assume that the volumes of the combining gases and of the product are measured under the same conditions of pressure and of temperature. (*See* p. 36.)

The Atomic Theory.—Certain theoretical conceptions which have since developed into what is now called the Atomic Theory, were first employed in chemistry by John Dalton, a Manchester chemist, in explanation of the regularity which has already been mentioned as the Law of Multiple Proportions (p. 43). The most important assumptions of this theory are stated in the following paragraphs.

Matter of all kinds is assumed to be composed of extremely minute, indivisible particles. These particles have been called *atoms*. Single atoms are so small as to be entirely beyond our powers of observation, even with the aid of the most powerful magnifying instruments. It is assumed that each element consists of atoms of one kind only, the kind, however, being different for every element. Every compound, on the other hand, is assumed to contain atoms of at least two different kinds—that is, atoms of at least two different elements—combined together chemically.

Estimates have been made as to the probable shape, size, and mass of atoms. At best, these must be regarded as approximations only. Experimental evidence points to the atoms of different elements possessing very different *weights*. The absolute mass is not known in the case of any atom, but the ratio to each other of the weights of the atoms of different elements can be determined with accuracy. A series of numbers which represent the *relative weights of the different kinds of atoms* has accordingly been drawn up. These numbers are *relative atomic weights*, and are as a rule simply called *atomic weights*. They will be discussed further on.

The aggregates of atoms which are produced when two or more unlike atoms combine together to form the smallest particles of a compound substance, are called *molecules*.* The most simply constituted molecule of a compound substance conceivable must necessarily consist of at least two unlike atoms. The molecules of carbonic oxide are believed to possess this simple constitution, and to consist each of one atom of carbon and one atom of oxygen. The next simplest conceivable constitution for the molecule of a compound is that it should consist of three atoms. In this case there are two possibilities :—

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* The word *molecule* is also applied, as will appear later, to aggregates consisting of two or more like atoms. A number of elementary gases and vapours are supposed to be made up of particles consisting of such groups of like atoms.

1. All three atoms may be different ; or
2. Two atoms may be of one kind and one of another.

The molecules of hydrocyanic acid are regarded as illustrating the first of these possibilities, and as consisting each of one atom of hydrogen, one of carbon, and one of nitrogen. The molecules of carbonic anhydride are regarded as illustrating the second, and as consisting each of one atom of carbon and two of oxygen. The molecules of many substances are supposed to present much greater complexity than these.

If we now compare carbonic oxide and carbonic anhydride in light of the atomic theory, we perceive the character of the explanation afforded by the theory for the observed facts concerning the quantitative relations to each other of the elements which form the two compounds (p. 43). Carbonic anhydride contains, for a given weight of carbon, exactly twice as much oxygen as carbonic oxide does. According to the atomic theory, this is because a molecule of carbonic anhydride contains for one atom of carbon, two atoms of oxygen, while a molecule of carbonic oxide contains for one atom of carbon, only one atom of oxygen.

Avogadro's Hypothesis.—When the facts which find expression in the Law of Gaseous Volumes—referring, as they do, to the combination of gases in simple rational proportions by volume to form products whose volumes are simply related to those of the gases which combine (p. 43)—are considered in connection with the idea of combination in simple atomic proportions according to Dalton's atomic theory, it becomes evident that there must be a simple relation between the volumes which gases occupy and the numbers of molecules present in these volumes. The nature of the relation is expressed by the Hypothesis of Avogadro, which is usually stated as follows :—

Equal volumes of all gases, under the same conditions of pressure and of temperature contain the same number of molecules.

In order to bring this very simple hypothesis into harmony with the observed facts, in all cases of combination of gases with each other, it is necessary to make the further assumption that even in the elementary gases, hydrogen, oxygen, nitrogen, and chlorine, the particles do not consist of single atoms, but of pairs of *like* atoms associated together to form *molecules*. In illustration of this matter, the case of the combination of hydrogen with chlorine furnishes a good example. One volume of hydrogen combines, as we have seen (p. 43), with one volume of chlorine to form two volumes of hydrochloric acid gas.* The volume of the product is here double that of either of the constituent gases, and therefore, according to Avogadro's Hypothesis, it contains twice as many molecules as either of those volumes. But every molecule of the resulting hydrochloric acid gas contains both hydrogen and chlorine, and, as there are twice as many molecules of it (each containing hydrogen and chlorine) as there were of the original hydrogen or of the original chlorine, each molecule of the two latter gases must have undergone division into two parts, and must therefore have consisted originally of not fewer than two atoms. There is evidence from another source that the molecules of the elementary gases do not consist of more than two atoms (p. 51).

Molecular Weights.—If, as Avogadro's Hypothesis assumes, equal volumes of all gases contain, under like conditions, the same number of molecules, then the differences in the weights of equal volumes of the various gases (as observed in making determinations of their relative densities) can only be accounted for by differences in the weights of the respective molecules of which the different gases consist. Accordingly the determination of the weights of equal volumes of different gases (under like conditions) should furnish numbers which stand to each other in the ratios of the weights of the molecules of the respective gases. But this is the determination which is actually made in ascertaining the relative densities of gases (p. 39); hence the numbers representing the relative densities of gases lead directly to the relative weights of the molecules of the gases.

As already stated, hydrogen is adopted as standard, with density = 1, for the comparison of the relative densities of other gases (p. 39). For the comparison of the relative molecular weights of gases hydrogen is also adopted as standard, but with molecular weight = 2. Hence, since the relative molecular weight is in all gases proportional to the relative density, the relative molecular weight of any gas is expressed by a number which is double that which expresses its relative density. Thus we have:

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* All measured under like conditions of pressure and of temperature.

	Relative Density.	Relative Molecular Weight.
Hydrogen . . .	1	2
Oxygen	15·88	31·76
Carbonic anhydride . .	21·835	43·67
Water vapour . .	8·94	17·88

and so on. The numbers designated relative molecular weights above are, as a rule, simply called *Molecular Weights.*

There are many substances of which the molecular weights are unknown, because they cannot be obtained in the gaseous state, and because certain other known methods of molecular weight determination cannot be applied to them.

Gramme Molecule.—For chemical purposes it is often convenient to deal with definite quantities of substances in grammes (but of course other definite weights could be employed), these quantities being based upon the molecular weights of the substances. When the number which expresses the molecular weight of any substance is considered as representing that same number of grammes, this quantity is called the "molecular weight in grammes" of the substance, or, more shortly, the *gramme molecule.* This is an important quantity with respect to each substance. (Compare pp. 48 and 53.) The gramme molecule of hydrogen weighs two grammes.

Atomic Weights.—If, in accordance with the atomic theory, molecules are aggregates of atoms, the weight of any given molecule must be made up of the separate weights of the atoms which compose it, and must, therefore, be equal to the sum of these separate weights. Hence, if it is possible to ascertain by any means the kinds of atoms, and the number of each kind, which go to constitute the molecules of any compound, it should likewise be possible to ascertain the relative weights of the atoms of each kind from the relative molecular weights of the compounds into whose composition they enter. It has, as a matter of fact, been found possible to obtain a great deal of information with respect to these matters. The means by which this information is obtained may be stated as follows.

1. By making use of the ordinary methods of chemical analysis, the kinds of atoms present in a compound can be determined; that is, the presence of the particular elements of which it is composed can be recognised, and the absence of others can be proved. By means of methods of quantitative analysis, the quantity of each element present in a given compound can be determined.

2. When the results of quantitative analyses are so tabulated as to show the weight of each element which is present in those quantities of compound substances which have already been described as their gramme molecules (p. 47), it is found that the gramme molecules of different compounds containing one element in common, contain quantities of that element which are related to each other in a very simple manner. The nature of this simple relation is exhibited in the subjoined tables. In each of these tables the numbers given in Column II. represent the weights in grammes of the substances named in Column I., which occupy, in the gaseous state, and under like conditions of pressure and of temperature, the same volume as two grammes of hydrogen. The numbers given in Columns III. and IV. show the composition, by weight, of the quantity of each substance which is set down in Column II.

I. Hydrogen, and Hydrogen Compounds.

Names of substances and weights of them, in grammes, which occupy, in the gaseous state and under like conditions, the same volume as two grammes of hydrogen.		The weights stated in Column II., of the respective substances named in Column I., contain the undernoted weights, in grammes, of—	
I. Names.	II. Weights.	III. Hydrogen.	IV. Other Elements.
Hydrochloric acid	36·19	1	Chlorine 35·19
Hydrobromic acid	80·35	1	Bromine 79·35
Hydrogen	2·00	2	...
Water	17·88	2	Oxygen 15·88
Hydrogen sulphide	33·82	2	Sulphur 31·82
Ammonia	16·94	3	Nitrogen 13·94
Hydrogen phosphide	33·80	3	Phosphorus 30·80
Marsh gas	15·91	1	Carbon 11·91
Olefiant gas	27·82	4	Carbon 23·82
Ethyl alcohol	45·70	6	Carbon 23·82 Oxygen 15·88
Ether	73·52	10	Carbon 47·64 Oxygen 15·88

II. OXYGEN, AND OXYGEN COMPOUNDS.

I. Names.	II. Weights.	III. Oxygen.	IV. Other Elements.	
Water	17·88	15·88	Hydrogen	2·00
Carbonic oxide . .	27·79	15·88	Carbon	11·91
Oxygen	31·76	31·76	...	
Carbonic anhydride .	43·67	31·76	Carbon	11·91
Sulphurous anhydride.	63·58	31·76	Sulphur	31·82
Sulphuric anhydride .	79·16	47·61	Sulphur	31·82
Nitric acid . . .	62·58	47·61	Hydrogen Nitrogen	1·00 13·91

III. CARBON COMPOUNDS.

I. Names.	II. Weights.	III. Carbon.	IV. Other Elements.
Carbonic oxide	27·79	11·91	15·88
Marsh gas	15·91	11·91	1·00
Ethane	29·82	23·82	6·00
Ethyl alcohol	45·70	23·82	21·88
Propane	43·73	35·73	8·00
Butane	57·61	47·61	10·00

IV. NITROGEN, AND NITROGEN COMPOUNDS.

I. Names.	II. Weights.	III. Nitrogen.	IV. Other Elements.
Ammonia	16·94	13·91	3·00
Nitric oxide	29·82	13·91	15·88
Nitric acid	62·58	13·94	48·64
Nitrogen	27·88	27·88	...
Nitrous oxide	43·76	27·88	15·88
Cyanogen	51·70	27·88	23·82

The simple relation to which reference has been made, is observed when the numbers which fall into Column III. in each table are considered. Thus the quantity of each substance which in the state of gas occupies the same volume, under the same conditions of pressure and of temperature, as 2 grammes of hydrogen (Column II.), does not in any case contain a smaller quantity of hydrogen than 1 gramme, of oxygen than 15·88 grammes, of carbon than 11·91 grammes, or of nitrogen than 13·94 grammes. Further, if the quantity of any compound noted in Column II. contains more than 1 gramme of hydrogen, it does not contain less than 2 grammes; if more than 2 grammes, not less than 3 grammes, and so on. Similarly in the case of oxygen compounds, if the quantity noted in Column II. contains more than 15·88 grammes of oxygen, it does not contain less than 31·76 grammes; if more than 31·76 grammes, then not less than 47·64 grammes, and so on. Regularity of the same simple kind is also observed with respect to the carbon and nitrogen compounds. The lists of compounds given here are intended to be illustrative only, and not exhaustive; since each table might have been greatly extended, and additional tables might have been given, embracing compounds of many other elements, when the same kind of regularity would have appeared throughout. In the case of each element, therefore, there appears in Column III. a minimum number, and all the numbers in this column for one and the same element are either this minimum number or multiples of it. It is concluded from the uniformity observed in this respect that the minimum number so obtained for each element represents (relatively to hydrogen assumed = 1) the smallest proportion by weight in which that particular element enters into combination—that this minimum number is, in short, the atomic weight of the element. *The atomic theory offers a sufficient explanation of the observed facts.* In the oxygen compounds, for example, the molecular weights of these compounds are made up of the weights of the atoms of the other elements present in the molecule besides oxygen, and of 1, 2, 3, etc. times the weight of one atom of oxygen. From this we conclude that the various molecules contain 1, 2, 3, etc. atoms of oxygen. It is clear that if a molecule contains any oxygen at all, it must contain not less than one atom of this element; if it contains more than one atom, it cannot contain fewer than two atoms, and so on. Exactly similar considerations may be applied to the compounds of other elements.

An examination of the facts contained in the tables, and of the conclusions drawn from them, justifies the view that there are in each molecule—

Of water	1 atom of	oxygen and	2 of	hydrogen
,, carbonic oxide . .	1 ,,	,,	1 ,,	carbon
,, nitrous ,, . .	1 ,,	,,	2 ,,	nitrogen
,, ammonia . . .	1 ,,	nitrogen	3 ,,	hydrogen
,, marsh gas . . .	1 ,,	carbon	4 ,,	,,

and so on.

In the tables referring to the compounds of hydrogen, oxygen, and nitrogen, the elements themselves have also been included. It will be noticed that the figures for them in Column III. of the respective tables are not the minimum numbers which have been arrived at as their atomic weights, but are double these numbers. From this it is concluded that their molecules must each consist of two, and of not more than two, atoms.

Law of Dulong and Petit.—This law states that the product of the atomic weight and the specific heat of solid elements is a constant number. This constant is called the *atomic heat,* and hence the law may also be stated thus :—

The atomic heats of all solid elements are equal.

The law does not hold quite accurately, the atomic heats of solid elements being found to differ from one another to some extent. They nearly all approximate moderately closely, however, to the number 6·4. A few examples are given below :—

Element.	Atomic Weight.	Specific Heat.	Atomic Weight × Specific Heat (= Atomic Heat).
Sodium . . .	22·88	·29	6·6
Iron . .	55·6	·112	6·2
Zinc . . .	64·91	·093	6·0
Tin . . .	118·2	·051	6·1
Mercury . .	198·8	·032	6·1

The determination of the specific heat is sometimes made in order to confirm the atomic weight of an element, since the constant 6·4 ÷ specific heat should give a quotient approximating to the atomic weight.

Chemical Notation.—A system of notation has been adopted for the purpose of shortly and concisely expressing the chief facts concerning chemical actions. This system is based upon the facts, and the theories deduced from these facts, which have been outlined in the preceding pages. The essential features of the system are explained in the following paragraphs.

1. *Symbols.*—For the purposes of the system, each element has had a symbol assigned to it. This symbol is usually the first letter, sometimes the first and a succeeding letter, of the English or of the Latin name for the element. Thus, H is the symbol for hydrogen, Fe (Ferrum) the symbol for iron, and so on. A list of the names of the elements, with their symbols and their atomic weights, is subjoined.

The Chief Elements mentioned in the British Pharmacopœia, with their Symbols and Atomic Weights.

Element.	Symbol.	Atomic Weight.	Element.	Symbol.	Atomic Weight.
Aluminium . .	Al	26·90	Lead (Plumbum) .	Pb	205·35
Antimony (Stibium)	Sb	119·00	Lithium . . .	Li	6·97
Arsenium . .	As	74·50	Magnesium . .	Mg	24·18
Barium . . .	Ba	136·40	Manganese . .	Mn	54·52
Bismuth . . .	Bi	207·30	Mercury (Hydrargyrum) . . .	Hg	198·80
Boron . . .	B	10·85	Nitrogen . .	N	13·94
Bromine . . .	Br	79·35	Oxygen . . .	O	15·88
Calcium . . .	Ca	39·71	Phosphorus . .	P	30·80
Carbon . . .	C	11·91	Platinum . .	Pt	193·30
Cerium . . .	Ce	139·20	Potassium (Kalium)	K	38·83
Chlorine . . .	Cl	35·19	Silver (Argentum) .	Ag	107·11
Chromium . .	Cr	51·74	Sodium (Natrium) .	Na	22·88
Copper (Cuprum) .	Cu	63·12	Sulphur . . .	S	31·82
Gold (Aurum) .	Au	195·70	Tin (Stannum) .	Sn	118·20
Hydrogen . .	H	1·00	Zinc . . .	Zn	64·91
Iodine . . .	I	125·90			
Iron (Ferrum) .	Fe	55·60			

For a *complete* list of the elements, with their symbols and atomic weights, *see* the Appendix.

The symbol for each element is employed to represent :—

a. The name of the element.

b. An atom of the element.

c. A definite weight, say grammes, of the element. This weight is the number representing the atomic weight of the element, taken as grammes; thus the symbol for hydrogen represents 1 gramme of hydrogen, because the atomic weight of hydrogen is 1; the symbol for iron, 55·6 grammes of iron, because the atomic weight of iron is 55·6; and so on.

2. *Formulæ.*—Symbols are employed in writing *formulæ.* A chemical formula usually consists of two or more symbols written side by side, as CO, which represents carbonic oxide.

When two or more atoms of the same kind are to be represented in a formula, this is done by writing a small figure to the right of, and on a somewhat lower level than, the symbol. The figure indicates the number of atoms to be represented. Thus the formula CH_4 represents a compound containing one atom of carbon and four of hydrogen. A small figure similarly placed after a portion of a formula which is enclosed within brackets, multiplies everything that is so enclosed. Thus $Ba(NO_3)_2$ indicates a substance in which an atom of barium is combined with twice the group NO_3.

A figure placed in front of a formula refers to the whole formula, and shows how many times the quantity represented by the formula is to be taken. Thus $3CH_4$ stands for three times the quantity of marsh gas represented by CH_4.

The formula for a substance represents in all cases:—

a. The kinds of atoms of which the substance consists.

b. The ratio of the number of atoms of each kind.

c. A definite weight, say grammes, of the substance. This weight is the sum of the atomic weights of the atoms represented by the formula, taken as grammes. It is called the *formula weight.*

In the case of gases, and of solids and liquids which can be converted into the gaseous state without decomposition, the formula further represents:—

d. The quantity of the substance which has already been referred to as the gramme molecule (p. 47).

e. A definite *volume* of the substance in the gaseous state. This volume is, in the case of each substance, when under the same conditions of pressure and of temperature, the same as that occupied by two grammes (the gramme molecule) of hydrogen. It is called the *gramme molecule volume.* When numerical expression is given to it, the conditions must be stated, since it varies with variations of pressure and of temperature. Under standard conditions of pressure and of temperature (*i.e.*, 760 mm. and 0° C., *see* p. 37), it measures 22·2 litres.

3. *Deduction of the Formula for a Compound from its Composition per cent.*—The results of quantitative chemical analyses of compounds are usually expressed in parts by weight per cent. of each constituent. From these results an *empirical formula* can be deduced. An empirical formula merely expresses the ratio of the number of atoms of each kind in the smallest whole numbers. A *molecular formula,* on the other hand, expresses the number of atoms of each kind which a molecule is assumed to contain.

The rule for the deduction of the simplest formula, is to divide the quantity per cent. of each element by the atomic weight of that element. The quotients stand to each other in the ratio of the numbers of atoms present in the compound. Thus the gas ethylene has the following composition per cent.:—

$$C, 85{\cdot}62 ; \quad H, 14{\cdot}38.$$

Dividing by the respective atomic weights, we get:—

$$85{\cdot}62 \div 11{\cdot}91 = 7{\cdot}19, \text{ and } 14{\cdot}38 \div 1 = 14{\cdot}38.$$

But $7{\cdot}19 : 14{\cdot}38 :: 1 : 2$; hence the carbon and hydrogen atoms are present in the ratio of 1 : 2, and the empirical formula is CH_2.

The molecular weight of ethylene, however, is found by experiment to be 27·82, while the formula CH_2 corresponds to the molecular weight 13·91; hence the molecular formula must be $(CH_2)_2$, that is, C_2H_4.*

N.B.—*From the composition per cent. alone the empirical formula can be deduced. The molecular formula can only be obtained when the molecular weight is also known.*

4. *Calculation of the Composition per cent. of a Substance from its Formula.*—First add up the formula weight of the substance. From this and the separate weights of the constituents the composition per cent. is obtained by simple proportion. Thus,

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* *See* first footnote to p. 38.

to find the composition per cent. of carbonic anhydride, CO_2:—

$$\begin{aligned} C &= 11{\cdot}91 \\ O_2 &= 31{\cdot}76\ (15{\cdot}88 \times 2) \\ &\overline{43{\cdot}67} = \text{Formula weight.} \end{aligned}$$

Here 43·67 parts by weight contain 11·91 of carbon.

$$\therefore\ 100 \text{ contain } \frac{11{\cdot}91 \times 100}{43{\cdot}67} = 27{\cdot}27.$$

Again, 43·67 parts by weight contain 31·76 of oxygen.

$$\therefore\ 100 \text{ contain } \frac{31{\cdot}76 \times 100}{43{\cdot}67} = 72{\cdot}73.$$

The composition per cent., therefore, is:—

$$C = 27{\cdot}27\ ;\ O = 72{\cdot}73.$$

5. *Equations.*—Formulæ are employed in writing chemical equations. These equations represent the changes which occur during chemical actions. Formulæ representing the quantity of each substance which enters into action are placed on one side, and formulæ representing the quantity of each product are placed on the other side of the sign of equality (=). Between the various formulæ on each side, signs of addition (+) are placed. These signs are not used in the same sense as in a mathematical equation; and a chemical equation is really only an equation in so far that all the materials represented on the one side must be accounted for in some form on the other side.

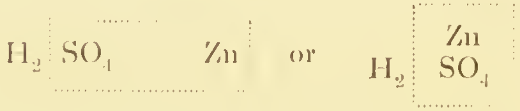
The chemical change which occurs when zinc is placed in dilute sulphuric acid is represented by the equation—

$$Zn + H_2SO_4 = H_2 + ZnSO_4$$

This equation, besides showing the nature of the rearrangement of atoms which takes place, indicates the proportions by weight in which the substances interact and the proportions of the products, since each symbol and formula has its own quantitative signification. It further indicates the volume of hydrogen which can be obtained from the weights of materials represented, since the formula for a gas represents not only a definite weight, but also a definite volume (at a given pressure and temperature) of the gas. Thus 64·91 grammes of zinc and 97·34 grammes of sulphuric acid yield 2 grammes of hydrogen and 160·25 grammes of zinc sulphate. The 2 grammes of hydrogen occupy 22·2 litres at 0°C and 760 mm.

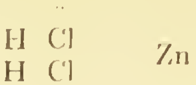
From such equations, calculations are readily made of the quantities of substances by weight or by volume obtainable from given quantities of materials.

Instead of writing formal equations to represent chemical actions, the student will often find it helpful and instructive to draw diagrams of a kind which show equally well the original form in which the various elements are brought into reaction, and the destination of the different atoms. For example, instead of writing the equation given above, the liberation of hydrogen by the interaction of zinc and dilute sulphuric acid can be sufficiently represented for most purposes by writing the formulæ for zinc and sulphuric acid either in the same line or one above the other, to show what substances interact, and then drawing a line to enclose the SO_4 of the sulphuric acid formula along with the Zn, and leaving the H_2 of the sulphuric acid formula outside, thus—



$$H_2\ \boxed{SO_4 \qquad Zn} \quad \text{or} \quad H_2\ \boxed{\begin{matrix} Zn \\ SO_4 \end{matrix}}$$

If the interaction of zinc with hydrochloric acid is to be represented, the diagram can be constructed thus—



$$\begin{matrix} H & Cl \\ H & Cl \end{matrix} \quad Zn$$

The construction of such diagrams is particularly useful in aiding the student to obtain an insight into numerous complicated interactions. Other examples will be given further on.

Equivalents (*Valency*).—Those quantities of different elements which are capable of playing the same part in chemical combination, are said to be *equivalent* to each other. For comparison of the equivalent weights of different elements, it is convenient to adopt a standard, and the standard chosen is 1 part by weight of hydrogen. The equivalent weights—or shortly, the *equivalents*—of other elements are capable of taking the place in combination of 1 part by weight of hydrogen (and frequently, moreover, of combining with the same weights of other elements that 1 part by weight of hydrogen combines with). Thus, in potassium chloride, KCl, 38·83 parts by weight of potassium take the place of the 1 part by weight of hydrogen contained in hydrochloric acid, HCl, hence the equivalent of potassium is 38·83. In calcium sulphate, $CaSO_4$, 39·71 parts by weight of calcium take the place of the 2 parts by weight of hydrogen contained in sulphuric acid, H_2SO_4, hence the equivalent of calcium is $\frac{39·71}{2} = 19·855$. In bismuth nitrate, $Bi(NO_3)_3$, 207·3 parts by weight of bismuth take the place of 3 parts by weight of hydrogen in three molecules of nitric acid, $3HNO_3$, hence the equivalent is $\frac{207·3}{3} = 69·1$, and so on.

The number expressing the equivalent weight is thus sometimes the same as the atomic weight, sometimes it is one-half the atomic weight, sometimes one-third, and so on. In other words, an atom of another element may be capable of taking the place of (or of combining with):—(*a*) one atom of hydrogen (an atom of potassium, for example); (*b*) two atoms of hydrogen (an atom of calcium, for example); (*c*) three atoms of hydrogen (an atom of bismuth, for example); and so on. The power possessed by the atoms of other elements, of replacing or of combining with different numbers of hydrogen atoms, has been called the *atomicity*, or *combining capacity*, or *quantivalence*, or, perhaps more commonly, the *valency* of the elements.

The number representing the valency of an element may be ascertained by observing the number of hydrogen atoms which it is capable of replacing, or with which it is capable of combining; also, by observing, for example, the number of atoms of chlorine with which it is capable of combining—each atom of chlorine being regarded as of the same valency as hydrogen, because each atom of chlorine combines with one atom of hydrogen.

For example, potassium (K), calcium (Ca), bismuth (Bi), and carbon (C), are regarded as *univalent*, *bivalent*, *trivalent*, and *quadrivalent*, respectively, because they form chlorine compounds represented by the formulæ KCl, $CaCl_2$, $BiCl_3$, CCl_4. In the case of carbon, CH_4 is also known.

With respect to the terms *equivalent* and *valency*, it is to be noted that they are applicable to radicals* as well as to atoms. Thus in calcium sulphate, $CaSO_4$, the radical SO_4 is equivalent to $(NO_3)_2$ in calcium nitrate, $Ca(NO_3)_2$, or to Cl_2 in calcium chloride, $CaCl_2$, since it is capable of combining with the same thing, *i.e.*, with one atom of calcium. SO_4 is a bivalent radical, while both NO_3 and Cl are univalent.

It is sometimes convenient to indicate the valency of a metallic radical by placing after it an appropriate number of dots, thus: $Mg^{\cdot\cdot}$; and similarly the valency of an acid radical may be indicated by an appropriate number of dashes, thus: PO_4'''.

Bases, Acids, and Salts.—In order to give the student some familiarity with these classes of chemical substances, and so to prepare him the better to understand the use of the words *base, acid, salt,* and the frequent references to these substances in the immediately succeeding portions of this Manual, it is desirable, before concluding the discussion of the general principles of chemistry, to make some general statements regarding these important groups.

Bases.—There are two principal classes of compounds which behave as bases, and possess in a more or less marked degree the properties of these substances, as described further on. These two classes embrace:—

1. The basic oxides and hydroxides of the metals. Examples—Calcium oxide (quicklime) CaO; calcium hydroxide (slaked lime) $Ca(OH)_2$; aluminium hydroxide $Al(OH)_3$; ferric oxide Fe_2O_3, etc.
2. Ammonia, NH_3, and the substituted ammonias (such as methylamine, NH_2CH_3; dimethylamine, $NH(CH_3)_2$; aniline, $NH_2C_6H_5$, etc.); also a large number of allied substances, including the natural alkaloids (such as morphine $C_{17}H_{19}NO_3$, H_2O; strychnine $C_{21}H_{22}N_2O_2$, etc.).

There are grounds for supposing that all substances which exhibit the characters of bases are hydroxides, and that those compounds belonging to the above two classes which are not hydroxides to begin with, must interact with water, so as to yield hydroxides before their capacity to behave as bases is developed. Thus it is probable that quicklime is not itself a base, but that the actual base is slaked lime (calcium hydroxide), which is formed by the interaction of quicklime with water—

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* The name *radical* is very often used in chemistry to designate a group of atoms which is common to a number of compounds, and is capable of being transferred from one compound to another without itself breaking up.

$$CaO + H_2O = Ca(OH)_2 ;$$

and that ammonia only attains basic properties when it has interacted with water to form ammonium hydroxide—

$$NH_3 + H_2O = NH_4OH.$$

Properties of Bases.—Those bases which dissolve easily in water yield solutions possessing an *alkaline reaction,* that is, their solutions exhibit the property possessed by solutions of the *alkalies* (potassium hydroxide, KOH, and sodium hydroxide, NaOH, which are themselves basic hydroxides, *see* pages 68 and 86) of turning red litmus paper blue, of browning yellow turmeric paper, etc. Solutions of some of the most easily soluble bases, such as potassium and sodium hydroxides, possess an unpleasant taste, resembling that of soapy water. (As a matter of fact, the taste of soapy water is chiefly due to the presence of one or other of these hydroxides in small quantity.)

Bases interact with acids to form *salts.* This statement is true generally, but it requires qualification in so far that there are some bases which (usually on account of their insoluble character) are not acted upon by certain acids. When bases interact with acids, the formation of salts is accompanied by the formation of water—

$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O ;$$
$$2Al(OH)_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 6H_2O ;$$
$$NH_4OH + HCl = NH_4Cl + H_2O.$$

Acids.—Three important classes of acids may be distinguished. These classes do not exhibit many prominent differences in character, although they differ considerably in their general chemical relations. The three classes are:—

1. Acids which may be regarded as derived from acid oxides, or acid anhydrides, by the action of water.

Thus sulphuric anhydride when treated with water yields sulphuric acid:

$$SO_3 + H_2O = H_2SO_4$$

(The majority of the more important acid anhydrides are, as the student will learn later, oxides of non-metallic elements.) All the acids belonging to this class contain oxygen.

2. Acids which do not contain any oxygen in their composition. The best examples are the halogen acids—Hydrochloric acid, HCl; hydrobromic acid, HBr; hydriodic acid, HI; and hydrofluoric acid, HF.
3. A large number of organic acids, all containing carbon, hydrogen, and oxygen, either along with, or without other elements. Examples—Oxalic acid, $H_2C_2O_4$; acetic acid, $H_4C_2O_2$; benzoic acid, $H_6C_7O_2$; chloracetic acid, $H_3C_2O_2Cl$, etc.

Properties of Acids.—The majority of acids dissolve readily in water. The aqueous solutions in most cases possess the *acid reaction*, that is, they redden blue litmus paper. They also possess a characteristic sour taste, as in the familiar cases of tartaric acid (the acid of unripe grapes), acetic acid (the acid present in vinegar), etc.

All acids contain hydrogen as an essential constituent. This hydrogen is replaceable, in some cases wholly, in some only partially, by metals, or by groups of atoms (radicals) which play the part of metals. The substances produced by such replacement are called *salts*. They are formed, as has already been stated, by the interaction of bases and acids, with the simultaneous production of water.

Salts.—Salts are compounds which may all be regarded as made up of metal, or of a radical which plays the part of metal—such metal or radical forming the *metallic* or *basic radical*—united to an atom, or group of atoms, which constitutes the *acid radical*. The metallic radical of the salt takes the place of the hydrogen of the acid, or of a part of it: the acid radical of the salt is common both to the salt and to the acid from which it is derived. In a sense, the acids are themselves salts. They closely resemble salts in several particulars, and they are frequently called *hydrogen salts*. An alkaloid unites with the *whole* of an acid.

Salts are produced in various other ways, as well as by the interaction of bases and acids. A common instance of this is seen in the formation of salts by the interaction of metals and acids. Thus the best way to prepare silver nitrate is to treat silver with nitric acid.

The following classes of salts are distinguished:—

Neutral Salts.—These salts when dissolved in water yield solutions which show neither the acid nor the alkaline reaction. Examples of neutral salts—Sodium chloride, $NaCl$; potassium sulphate, K_2SO_4; etc.

Normal Salts.—This name is applied to salts which are formed when the *whole* of the replaceable hydrogen of an acid is replaced by a metal. Normal salts are frequently neutral also, but they are not necessarily so. Examples of normal salts—Potassium sulphate, K_2SO_4; sodium carbonate, Na_2CO_3.

Acid Salts.—Salts which contain some of the replaceable hydrogen of the original acid unreplaced by metal, are called acid salts. They are intermediate in composition between the acid and the normal salt. Thus potassium hydrogen sulphate, $KHSO_4$ (an acid salt), is intermediate between sulphuric acid, H_2SO_4, and normal potassium sulphate, K_2SO_4. Acid salts possess the *acid character*, in so far that they still contain hydrogen of the original acid, which is replaceable by metal to form a normal salt. They do not, however, necessarily show the acid reaction with litmus.

Basic Salts.—Salts which are intermediate in composition between basic oxide or hydroxide and normal salt, are called basic salts. Thus bismuth oxychloride, $BiOCl$ (a basic salt), is intermediate between basic bismuth oxide, Bi_2O_3, and normal bismuth chloride, $BiCl_3$. Basic salts possess the basic character, in so far that they still contain oxygen of the basic oxide, or hydroxyl (OH) of the basic hydroxide, which is replaceable by an acid radical to form a normal salt. A large number of basic salts are insoluble in water, and cannot therefore show any reaction with litmus.

Basicity of Acids, and Acidity of Bases.—Acids are called monobasic, dibasic, tribasic, etc., according as they contain in their molecules one, two, three, etc., hydrogen atoms displaceable by metals. Polybasic acids contain several displaceable hydrogen atoms. Bases are called mono-acid, di-acid, tri-acid, etc., according as the acid radical from one, two, three, etc., molecules of a monobasic acid enters into the composition of the normal salts derived from them.

Equations illustrating basicity of acids:

$$HNO_3 + KOH = KNO_3 + H_2O$$
$$H_2SO_4 + 2KOH = K_2SO_4 + 2H_2O$$
$$H_3PO_4 + 3KOH = K_3PO_4 + 3H_2O$$

Equations illustrating acidity of bases:

$$KOH + HCl = KCl + H_2O$$
$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O$$
$$Bi(OH)_3 + 3HCl = BiCl_3 + 3H_2O$$

Electrolysis.—When a current of electricity is passed through a dilute solution of sulphuric acid, by introducing into the solution *electrodes* (which may consist conveniently of strips of platinum foil) connected with the wires leading from a sufficiently powerful battery, hydrogen is given off at the electrode connected with the negative pole of the battery, and oxygen at that connected with the positive pole. These gases are given off in the proportions in which they combine to form water, and the experiment at first sight appears to be, and is sometimes simply called, the *electrolysis* (that is, the decomposition by a current of electricity) of water. The sulphuric acid, however, although its quantity remains the same at the end of the experiment as it was at the beginning, obviously plays an important part in the process, because in its absence scarcely any current passes, and correspondingly little water is decomposed. The nature of the chemical change which takes place may be represented as, in the first place, the liberation, from the acid, of hydrogen at the one electrode and of the acid radical—the group SO_4—at the other. But the acid radical (SO_4) is unknown as a separate substance, and is probably incapable of existence as such; hence, at the moment of its liberation, it interacts with water of the solution, taking its hydrogen to form sulphuric acid again, and liberating its oxygen. These changes may be illustrated diagrammatically as follows:—

(*a*) As the first result of electrolysis, H_2SO_4 yields :—

At the negative electrode.	At the positive electrode.
HH *	$[SO_4]$

(*b*) Further change :

$[SO_4]$ and H_2O† give H_2SO_4 and O*

Accordingly, the final result of the change is that water molecules are, by this indirect means, decomposed into hydrogen and oxygen, while the sulphuric acid remains in undiminished quantity at the end of the experiment.

A case nearly analogous with the preceding one is that of the electrolysis of a solution of sodium sulphate. In this case also, hydrogen and oxygen are given off in the proportions in which they are present in water. It may be represented that the sodium sulphate is first separated into sodium and the acid radical of the sulphates, Na_2SO_4 yielding :

At the negative electrode.	At the positive electrode.
Na Na	$[SO_4]$

But in this instance the sodium as well as the acid radical enters into a new reaction with water of the solution and the following further changes occur :

2Na and $2H_2O$ give 2NaOH and H_2.	$[SO_4]$ and H_2O give H_2SO_4 and O.

In light of the foregoing mode of representing the electrolysis of sodium sulphate, it would appear that sodium hydroxide is produced at the negative pole in addition to the hydrogen ; and that sulphuric acid is produced at the positive pole in addition to the oxygen. This is indeed found to be the case, and may easily be demonstrated by testing the liquid in the immediate neighbourhood of the two electrodes,

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* Single atoms of hydrogen and of oxygen liberated in this way at the respective electrodes unite with each other in pairs to form molecules of gaseous hydrogen, H_2, and oxygen, O_2 (or the oxygen atoms may to some extent unite in groups of three to form molecules of ozone, O_3 ; *see* Index).

† The group (SO_4) may also be regarded as interacting with two water molecules to form H_2SO_4 and two (OH) groups, which latter are then supposed to interact, with the formation of water and oxygen :

$$[SO_4] \quad \begin{matrix} HOH \\ HOH \end{matrix} \quad H_2SO_4 \quad \begin{bmatrix} OH \\ OH \end{bmatrix}; \text{ and } \begin{bmatrix} OH \\ OH \end{bmatrix} \quad H_2O \quad O$$

by means of litmus papers, during the passage of the current. Whilst the sodium sulphate solution is itself *neutral*, the liquid at the negative pole is found to be *alkaline*, and that at the positive pole is found to be *acid*. It is to be noted, moreover, that the quantity of sodium hydroxide formed at the negative electrode is exactly the quantity required to interact with the whole of the sulphuric acid formed at the positive electrode, to form sodium sulphate again (neutral solution) in accordance with the equation,

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$

so that when the solution is thoroughly mixed up sodium sulphate is present in it in undiminished quantity.

Other salts in aqueous solution (or in the fused state if they stand fusion without undergoing decomposition) can also be electrolysed. The metal of the salt, or that which plays the part of metal, is separated at the negative electrode, and the acid radical at the positive electrode. Substances which are capable of decomposition by electrolysis are called *electrolytes*. When the first products of the electrolysis are capable of existence in the conditions under which they are produced, then these are the products obtained. Secondary changes are, however, of frequent occurrence, as in the foregoing illustrations.

In regard to their electrolysis, the acids (hydrogen salts) behave in a manner exactly analogous with the behaviour of other salts.

The positive electrode is often called the *anode*, and the negative electrode the *cathode* (ανα, *ana*, upward; κατα, *kata*, downward; ὁδος, *hodos*, way). Metals and hydrogen are set free at the cathode, and acid radicals and oxygen at the anode.

It has been found that the quantity of an electrolyte which undergoes decomposition by electrolysis is directly proportional to the amount of current passed through it. Further, it has been found that the quantities of hydrogen, and the quantities of oxygen liberated in a given time from dilute solutions of sulphuric acid, of sodium sulphate, and of potassium sulphate, when the current is passed simultaneously through all three solutions, are the same for each solution. Similarly the quantities of copper separated from two or more different cupric salts under like conditions are identical: and the same kind of regularity holds good for other metals and acid radicals.

In recent years electrolytic methods have been extensively introduced for the technical production of chemical compounds, for the separation of metals, etc. References to the preparation of a number of substances by these methods, are made in various places in this Manual. See, for example, under potassium chlorate, sodium hydroxide, iodoform, aluminium, sodium, etc.

Oxygen and hydrogen, when liberated from combination in immediate contact with substances with which they are capable of interacting to yield products of *oxidation* and *reduction* (reduction = deoxidation or removal of oxygen), are found to be much more active towards these substances than they are if prepared in separate vessels and subsequently brought into contact with them. The special activity of such *nascent* (*i.e.*, newly formed) oxygen and hydrogen, has been attributed to the action of *atoms* of these elements, which enter into other reactions without combining in pairs to form oxygen and hydrogen *molecules*. Various electrolytic and other oxidations, reductions, etc., are apparently due to the action of nascent oxygen, nascent hydrogen, nascent chlorine, etc. In a number of cases in later parts of the Manual, where equations are given in which the action of nascent hydrogen, etc., is represented, the atomic symbols, H, O, etc., are used instead of the molecular formulæ, H_2, O_2, etc.

The student is recommended to read the foregoing paragraphs on the General Principles of Chemical Philosophy carefully once or twice, then to study (experimentally, if possible) the following pages, returning to and reading over the General Principles from time to time, until they are thoroughly comprehended.

QUESTIONS AND EXERCISES

What do you understand by chemical changes?—Give examples of chemical and physical changes.—Mention some of the chief phenomena which accompany typical cases of chemical change.—What is the difference between an element and a compound?—What do you understand by the term "chemical affinity"?—Name the chief laws of chemical combination.—State the law of constant proportions.—State the law of multiple proportions.—State the law of gaseous volumes.—Give an outline of the atomic theory, explaining what is understood by the terms "atom" and "molecule."—What is Avogadro's hypothesis?—Explain why hydrogen molecules are assumed to consist of two hydrogen atoms each.—What relation exists between the relative densities and the molecular weights of gases?—What is the "gramme molecule"?—Explain how Avogadro's hypothesis may be applied in the fixing of atomic weights.—State the law of Dulong and Petit, and explain how it may be of service in fixing atomic weights.—Enumerate the functions of a chemical symbol and of a chemical formula.—Write equations representing the formation of hydrogen by the interaction of zinc with hydrochloric acid and with sulphuric acid.—Mention the characters of bases and of acids, and describe the general nature of the interaction of bases and acids in forming salts.—What are neutral salts, normal salts, acid salts, basic salts? Give examples.—Define electrolysis, electrolyte, electrode.—What do you understand by "nascent" hydrogen?—Name some important substances which are now prepared on the manufacturing scale by electrolytic methods.

THE ELEMENTS AND THEIR COMPOUNDS

Having thus obtained a general idea of the nature of some of the non-metallic elements which have special interest for the medical and pharmaceutical student, and of the fundamental principles of chemistry, we may pass on to consider in detail the relations of the elements, both non-metallic and metallic, to each other. The elements themselves, in the free condition, are seldom used in medicine, being nearly always in combination—bound together by the force of chemical affinity; in this combined condition, therefore, they must be studied, inorganic combinations first, organic afterwards. Most compounds met with in the mineral kingdom may be regarded as containing two parts or radicals:—the one usually metallic; the other commonly a non-metallic, simple or complex, acid radical. In the following pages the metallic radicals will be considered first, the acid radicals afterwards. Each radical will be studied from two points of view, the synthetical and the analytical; that is to say, the properties of an element on which the preparation of its compounds depends will be illustrated by descriptions of actual experiments, and thus a knowledge of the principles of chemistry and of their applications to medicine and pharmacy be acquired; then the reactions by which the element is detected, though combined with other substances, will be performed, and so the student will be instructed in qualitative analysis. Synthetical and analytical reactions are, in truth, frequently identical, the object with which they are performed giving them synthetical interest on the one hand, or analytical interest on the other.

A good knowledge of chemistry may be acquired synthetically by preparing considerable quantities of the salts of the different metals, or analytically by going through a course of pure qualitative analysis. But the former plan demands a larger expenditure of time than most students have to spare, while under the latter system pupils generally lose sight of the synthetical importance which attaches to analytical reactions. Hence the more useful system, now offered, of studying each metal, etc., from both points of view, time being economised by the operator preparing only small specimens of compounds.

Note.—As a general rule, throughout this Manual paragraphs describing experiments to be performed are distinguished from paragraphs containing matter merely to be read, by being printed in somewhat more widely-spaced type.

THE METALLIC RADICALS

POTASSIUM: K. Atomic weight, 38·83

Occurrence, etc.—The chief sources of the potassium salts are the chloride found at Stassfurt, in Prussia, combined with magnesium chloride in the mineral *Carnallite*, $KCl,MgCl_2,6H_2O$; *Kainite*, a double potassium and magnesium sulphate with magnesium chloride, $K_2SO_4,MgSO_4,MgCl_2,6H_2O$, also occurring among the Stassfurt minerals; the nitrate found in soils, especially in warm countries; and the compounds of potassium existing in plants. The potassium salts present in plants are converted chiefly into carbonate when the wood or other parts are burnt to ashes. If the ashes be lixiviated with water, and the solution evaporated to dryness, the residue when fused constitutes *crude potashes*. The residue calcined on the hearth of a reverberatory furnace till white, gives the product termed *pearlash*, which is impure potassium carbonate. Large quantities of potassium carbonate are thus produced in North America and Russia, and, latterly, from the sugar beetroot marc, in France. Nearly all other potassium compounds are made from the native chloride, or from the carbonate which has been purified by treating pearlash with its own weight of distilled water, filtering, and evaporating the solution so formed just to dryness, while it is kept briskly agitated. Exceptions occur in potassium nitrate, and in cream of tartar (*Potassii Tartras Acidus*, B.P.), which is the more or less purified natural potassium salt of the grape vine. Potassium, in the form of one or other of its compounds, is a constituent of between forty and fifty chemical or galenical preparations of the British Pharmacopœia.

Preparation.—Potassium itself is isolated by distilling a mixture of potassium carbonate and charcoal at a very high temperature, or by Castner's method (*see* Sodium). It rapidly undergoes oxidation in the air, hence is usually kept below the surface of mineral naphtha which protects it from oxidation. It crystallizes in octahedra.

Potassium carbonate (*Potassii Carbonas*, B.P.), is a white crystalline or granular powder, insoluble in alcohol but very soluble in water, yielding a solution which is alkaline and caustic to the taste. It rapidly liquefies in the air through absorption of moisture. It loses all water at a red heat.

Potassium Hydroxide. Caustic Potash

Experiment 1.—Boil together for a few minutes, in a basin, ten to twenty grains of potassium carbonate, K_2CO_3, and a like quantity of calcium hydroxide (slaked lime), $Ca(OH)_2$, with a small quantity of water. Set the mixture aside in a closed vessel till all solid matter has subsided.

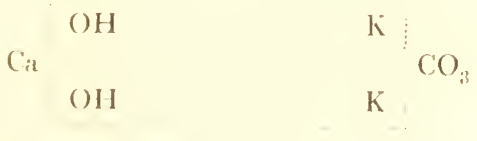
The clear liquid is a solution of potassium hydroxide or caustic potash, KOH. Made of a prescribed concentration (27 grains in each fluid ounce, or nearly 6 per cent.) it forms *Liquor Potassæ*, B.P.

The mixture is known to have been boiled long enough when a little of the clear liquid, poured into a test-tube and warmed, gives no effervescence on the addition of an acid (sulphuric, hydrochloric, or acetic)—a test the mode of action of which will be explained hereafter.

Solid Caustic Potash.—Solution of caustic potash evaporated to dryness in a silver or clean iron vessel, and the residue fused and poured into moulds, constitutes caustic potash (*Potassa Caustica*, B.P.). It often contains chlorides, detected by means of silver nitrate; and sulphates, detected by means of a barium salt; as described subsequently in connection with hydrochloric and sulphuric acids.

Representing Chemical Changes by means of Equations and Diagrams.—It is desirable that the student should endeavour to represent each chemical change that comes under his notice by means of an equation or diagram. The mode of constructing such equations and diagrams has been explained already, and the student is aware that the chief data required for their construction are the formulæ of the various substances which enter into and are produced by the particular changes under consideration. Thus, solution of potassium carbonate and calcium hydroxide interact when boiled together to produce calcium carbonate and potassium hydroxide. It is necessary to know the formulæ for all these substances before an equation or diagram can be constructed to represent the interaction. The required formulæ are respectively, K_2CO_3, $Ca(OH)_2$, $CaCO_3$, and KOH. A few moments' reflection should enable the student to perceive that in order that $CaCO_3$ may be built up from $Ca(OH)_2$ and K_2CO_3, the latter of these two must give up K_2 while the former must give up $(OH)_2$; and, further, in order that the K_2 and the $(OH)_2$ may be conceived as forming a substance having the formula KOH, it must be supposed that these materials unite to form two KOH groups.

A diagram representing the change can then be constructed easily thus:—



or an equation written thus:—

$$Ca(OH)_2 + K_2CO_3 = CaCO_3 + 2KOH$$

The interaction represented by the above diagram and equation is an instance of that kind of chemical change commonly called *double decomposition*, the two metallic radicals exchanging places. The name *metathesis* (μετὰ, *meta*, beyond, and θέσις, *thesis*, a placing) is sometimes given to interactions of this description.

At the same time that the student is constructing these diagrams and equations for himself, he will carefully bear in mind that each formula stands for a definite quantity of the substance which it represents; and that, by adding up the quantities thus indicated by the formulæ constituting an equation, he can readily ascertain the proportions by weight in which the substances interact and result from interaction.

Sulphurated Potash

Experiment 2.—Into a test-tube put a few grains of a mixture of *previously dried* potassium carbonate and half its weight of sulphur. Heat the mixture gradually until it no longer effervesces. The resulting fused mass poured on a slab and quickly bottled is sulphurated potash (*Potassa Sulphurata*, B.P.).

$$\underset{\substack{\text{Potassium}\\\text{carbonate}}}{3K_2CO_3} + \underset{\text{Sulphur}}{4S_2} = \underset{\substack{\text{Potassium}\\\text{thiosulphate}}}{K_2S_2O_3} + \underset{\substack{\text{Potassium}\\\text{trisulphide}}}{2K_2S_3} + \underset{\substack{\text{Carbonic}\\\text{anhydride}}}{3CO_2}$$

As met with in pharmacy, this substance is not a single definite chemical compound, but a mixture of several; in short, its chemical character is well indicated by its vague name. When fresh, and if carefully prepared with the official proportions of dry ingredients, it is of the colour of liver (whence the old name "liver of sulphur"), and consists, as shown by J. Watts, of the salts mentioned in the foregoing equation, together with a little undecomposed potassium carbonate, with perhaps higher potassium sulphides (K_2S_4 and K_2S_5). By rapidly absorbing oxygen from the air, it soon becomes green and yellow, potassium sulphite, K_2SO_3, and sulphate, K_2SO_4, being successively formed, and ultimately a useless mass of a dirty white colour results, consisting of potassium sulphate and thiosulphate, with generally some carbonate and free sulphur. Moreover, if overheated in manufacture, the potassium thiosulphate is decomposed into sulphate and pentasulphide ($4K_2S_2O_3 = 3K_2SO_4 + K_2S_5$). About fifty per cent. of the freshly-made preparation should be soluble in alcohol (90 per cent.). It is occasionally employed in the form of ointment.

The complicated nature of the interactions that take place in this experiment will probably cause failure in any attempt by the student to represent these by means of a diagram without the aid of the printed equation already given. He may therefore content himself, in this case, by introducing into his note-book a diagram founded directly on the equation, and on the numbers of molecules there stated.

In preparing large quantities of sulphurated potash, the test-tube is replaced by an earthenware *crucible* (possibly from *crux*, a cross, for originally a cross was impressed upon the melting-pot used by alchemists and goldsmiths; others derive the word from *crux*, an instrument of torture, the sense here being symbolical).

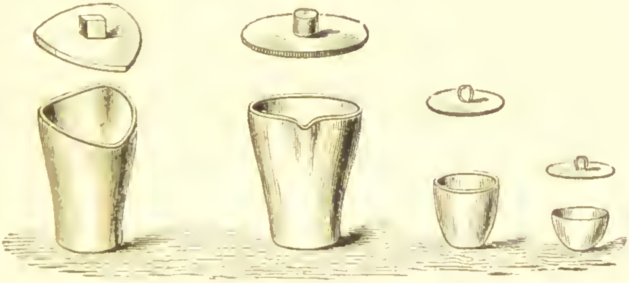


FIG. 16.—Crucibles of various forms.

Heating crucibles.—Crucibles of a few ounces capacity may be heated in an ordinary fire. Larger ones require a furnace. Even the smaller ones are more conveniently and quickly heated in a furnace. Half-ounce or one-ounce experimental porcelain crucibles may be heated in a spirit- or gas-flame, the flame of the Bunsen burner already described being generally the most suitable.

Potassium Acetate

Experiment 3.—Place twenty grains or so of potassium carbonate in a small porcelain dish, and *saturate* (*satur*, full) with acetic acid; that is, add acetic acid as long as effervescence is produced; the resulting liquid is a slightly acid solution of potassium acetate. Boil off most of the water in an open dish (*see* figs. 17 and 18, p. 73), stirring with a glass rod[*] to assist the escape of water vapour, and thereby prevent spirting; a white salt remains, which fuses on the further careful application of heat: this is the official potassium acetate (*Potassii Acetas*, B.P.). If fused in an open vessel, the acetate is liable to become slighty charred and discoloured; this is prevented by transferring the solid residue to a test-tube or flask before finally fusing. Potassium acetate forms a white deliquescent foliaceous satiny mass, neutral to test-paper, and wholly soluble in alcohol. A ten per cent. solution in water forms "Solution of Potassium Acetate," B.P.

$$\underset{\substack{\text{Potassium}\\\text{carbonate}}}{K_2CO_3} + \underset{\substack{\text{Acetic}\\\text{acid}}}{2HC_2H_3O_2} = \underset{\substack{\text{Potassium}\\\text{acetate}}}{2KC_2H_3O_2} + \underset{\text{Water}}{H_2O} + \underset{\substack{\text{Carbonic}\\\text{anhydride}}}{CO_2}$$

Explanation of formulæ.—The formula for acetic acid (hydrogen acetate) is $HC_2H_3O_2$, and that for potassium acetate, $KC_2H_3O_2$. The univalent group or radical, $C_2H_3O_2$, is common to all acetates. A more extended formula for potassium acetate, indicating the possible arrangement of the atoms in the molecule, is $CH_3{\cdot}COOK$.

Diagram of the reaction.—The nature of the above operation is indicated by an *equation;* it (and succeeding reactions) may be expressed in the student's note-book as a *diagram*, and, if possible, without the aid of the above equation.

Note.—The foregoing reaction has a general as well as a special interest. It represents one of the commonest methods of forming salts, namely, the decomposition of a carbonate by interaction with an acid. Carbonates added to acetic acid yield acetates, to nitric acid nitrates, to sulphuric acid sulphates. Many illustrations of this general process occur in pharmacy.

Evaporation of water from a liquid is best conducted in wide shallow vessels rather than in narrow deep ones, as the steam can thus quickly diffuse into the air and rapidly be conveyed away; hence a small round-bottomed basin, heated as shown in fig. 17, is far more suitable than a test-tube for such operations. On the manufacturing scale, iron, or iron lined with enamel, or semi-porcelain, copper, tinned copper, or solid tin pans are used. Up to 12 or 18 inches diameter, porcelain dishes may be employed. Small dishes may be supported by retort stands (fig. 17), larger by cylinders (fig. 18), to which the dish is, if less in diameter than the cylinder, adapted by such flat rings or diaphragms as are shown in the figure.

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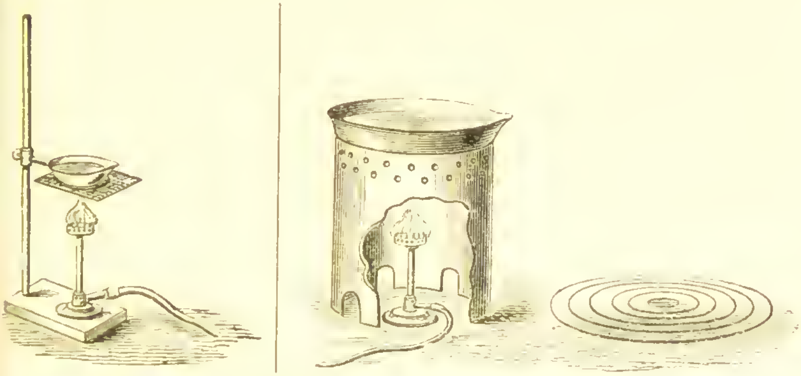
[*] Glass rod is usually purchased in lengths of 5 or 6 feet. These may be cut into convenient pieces of from 6 to 12 inches long (*see* p. 6), sharp ends being rounded off by holding the extremities in a flame for a few minutes.



Figs. 17 and 18.—Evaporation from Small and Large Basins.

Potassium Hydrogen Carbonate. Potassium Bicarbonate

Experiment 1.—Make a concentrated solution of potassium carbonate by heating in a test-tube a mixture of several grains of the salt with rather less than an equal weight of water. Through the cool solution pass carbonic anhydride, slowly but continuously; after a time a white crystalline precipitate of potassium hydrogen carbonate, or potassium bicarbonate, $KHCO_3$ (*Potassii Bicarbonas*, B.P.), will be formed.

$$\underset{\substack{\text{Potassium}\\\text{carbonate}}}{K_2CO_3} + \underset{\text{Water}}{H_2O} + \underset{\substack{\text{Carbonic}\\\text{anhydride}}}{CO_2} = \underset{\substack{\text{Potassium}\\\text{bicarbonate}}}{2KHCO_3}$$

Generate the carbonic anhydride by adding hydrochloric acid, diluted with twice its bulk of water, to a few fragments of marble or other carbonate contained in a test-tube or small flask, and conduct the gas into the solution of potassium carbonate through a glass tube, bent to a convenient shape and fitted to the test-tube or flask by means of a cork in the usual way (*see* fig. 10, p. 22, though no heat is necessary). The tube may be replenished with marble or acid, or both, when the evolution of gas is becoming slow. In working on any larger quantity than a few grains of the carbonate, a wide delivery-tube should be employed; or if a narrow one is employed, the end of it must occasionally be cleared from any bicarbonate that may have been deposited in it. A more economical arrangement of the apparatus employed in this process will be described under the corresponding sodium salt (p. 87).

Deposition of the bicarbonate explained.—Potassium bicarbonate is to a certain extent soluble in water; but as it is less so than the potassium carbonate, and as a *saturated* solution of the latter is employed, the precipitation of a part of the bicarbonate inevitably occurs. In other words, the quantity of water present is sufficient to dissolve the carbonate, but insufficient to retain in solution the whole of the bicarbonate formed during the action.

Properties.—Prepared on the large scale, potassium bicarbonate occurs in colourless, non-deliquescent rhombic prisms; it has a saline, feebly alkaline, non-corrosive taste. Heated to redness, it loses about 31 per cent. of its weight, and is converted into potassium carbonate, water, and carbonic anhydride.

$$\underbrace{2KHCO_3}_{198{\cdot}76} = \underbrace{K_2CO_3}_{137{\cdot}21} + \underbrace{H_2O}_{17{\cdot}88} + \underbrace{CO_2}_{43{\cdot}67}$$

The foregoing equation and accompanying weights (*see* page 55) show how potassium bicarbonate loses 31 per cent. (17·88 + 43·67 in 198·76) when completely decomposed by heat.

Notes on Nomenclature.—The prefix *bi-* in the name "potassium bicarbonate," serves to recall the fact that for the same quantity of potassium this salt contains *twice* as much carbonic acid radical as is present in the carbonate. The salt is really a "potassium and hydrogen carbonate," $KHCO_3$, and is intermediate between potassium carbonate, K_2CO_3, and hydrogen carbonate, or true carbonic acid [H_2CO_3]. It is “potassium acid carbonate” or “potassium hydrogen carbonate,” and is an acid salt, inasmuch as it contains hydrogen which is displaceable by metal to form a normal salt, although it is not acid to the taste.

Salts whose specific names end in the syllable “*ate*” (carbon*ate*, sulph*ate*, etc.) are in general conventionally so termed when they contain the radical (or characteristic group of elements) of an acid whose name ends in “*ic*,” and from which acids they have been or may be formed. Thus the syllable “*ate*,” in the words sulph*ate*, nitr*ate*, acet*ate*, carbon*ate*, etc., indicates that the respective salts contain the radical of an acid whose name ends in *ic*, the previous syllables sulph-, nitr-, acet-, carbon-, indicating what that acid is—sulphuric, nitric, acetic, or carbonic. Occasionally a letter or syllable is dropped from or added to a word to render the name more euphonious ; thus the sulphuric radical forms *sulphates*, not sulphurates, and the tartaric radical yields *tartrates* not tartarates.

Potassium Citrate

Experiment 5.—Dissolve a few grains or more of potassium carbonate in water, and add citric acid, $H_3C_6H_5O_7$, until it no longer causes effervescence. The resulting liquid is a solution of potassium citrate, $K_3C_6H_5O_7$. Evaporate to dryness, in an open dish, cautiously so as to avoid charring ; a pulverulent or granular residue is obtained, which is the official potassium citrate (*Potassii Citras*, B.P.), a white deliquescent powder.

$$\underset{\substack{\text{Potassium}\\\text{carbonate}}}{3K_2CO_3} + \underset{\text{Citric acid}}{2H_3C_6H_5O_7} = \underset{\substack{\text{Potassium}\\\text{citrate}}}{2K_3C_6H_5O_7} + \underset{\text{Water}}{3H_2O} + \underset{\substack{\text{Carbonic}\\\text{anhydride}}}{3CO_2}$$

Citrates.—The citric radical, $C_6H_5O_7'''$, which with three atoms of hydrogen forms citric acid, and with three of potassium forms potassium citrate, is a trivalent group. An extended formula for citric acid is $C_3H_4\cdot OH\cdot(COOH)_3,H_2O$, that for potassium citrate being $C_3H_4\cdot OH\cdot(COOK)_3,H_2O$. The chemistry of citric acid and other citrates will be described subsequently.

Potassium nitrate, KNO_3 (*Potassii Nitras*, B.P.), and *Potassium sulphate*, K_2SO_4 (*Potassii Sulphas*, B.P.). These salts could also be made by neutralizing nitric acid, HNO_3, and sulphuric acid, H_2SO_4, respectively, with potassium carbonate. Ordinarily they are not made in this way,—the nitrate occurring, as already stated, in nature, and the sulphate being obtained as a by-product in many operations. Both salts will be alluded to later in connection with nitric acid.

Potassium Tartrate

Experiment 6.—Place a few grains of potassium carbonate in a test-tube with a little water, heat to the boiling-point, and then add acid potassium tartrate, $KHC_4H_4O_6$, till there is no more effervescence; a solution of normal potassium tartrate (*Potassii Tartras*, B.P.), $K_2C_4H_4O_6$, results. Prismatic crystals may be obtained on concentrating the solution by evaporation and setting the hot liquid aside. Larger quantities are made in the same way, 20 parts of potassium hydrogen tartrate and 9 of potassium carbonate (with 50 of water) being about the proportions necessary for neutrality.

$$\underset{\substack{\text{Potassium}\\\text{hydrogen tartrate}}}{2KHC_4H_4O_6} + \underset{\substack{\text{Potassium}\\\text{carbonate}}}{K_2CO_3} = \underset{\substack{\text{Potassium}\\\text{tartrate}}}{2K_2C_4H_4O_6} + \underset{\text{Water}}{H_2O} + \underset{\substack{\text{Carbonic}\\\text{anhydride}}}{CO_2}$$

Potassium tartrate is slightly deliquescent, and is soluble in about four parts of boiling water.

Tartrates.—The bivalent radical $C_4H_4O_6''$ is characteristic of all tartrates; hence the formula of hydrogen tartrate, or tartaric acid, is $H_2C_4H_4O_6$; that of potassium tartrate is $(K_2C_4H_4O_6)_2,H_2O$; of the intermediate salt, acid potassium tartrate (cream of tartar), $KHC_4H_4O_6$. If the acid tartrate of one alkali-metal and the carbonate of another interact, a neutral tartrate results, which contains both metals, as seen in Rochelle salt, $KNaC_4H_4O_6,4H_2O$ (*Soda Tartarata*, B.P.; *Potassii et Sodii Tartras*, U.S.P.) More extended formulæ of these salts, indicating constitution, are :—

$$\underset{\text{Hydrogen tartrate}}{(CHOH)_2(COOH)_2} \qquad \underset{\text{Potassium tartrate}}{[(CHOH)_2(COOK)_2]_2,H_2O}$$

$$\underset{\text{Hydrogen potassium tartrate}}{(CHOH)_2COOH{\cdot}COOK} \qquad \underset{\text{Sodium potassium tartrate}}{(CHOH)_2COONa{\cdot}COOK,4H_2O}$$

Acid Salts (*e.g.* $KHC_4H_4O_6$), that is, salts intermediate in composition between a normal salt (*e.g.* $K_2C_4H_4O_6$) and an acid (*e.g.* $H_2C_4H_4O_6$), are frequently met with. All acid radicals, except those which are univalent, may be concerned in the formation of such acid salts. *See* p. 61.

Potassium Iodide

Experiment 7.—Into a solution of potassium hydroxide heated in a test-tube, flask, or evaporating-basin, according to quantity, stir a little solid iodine. The deep colour of the iodine disappears entirely. This is due to the formation of the colourless salts, potassium iodide, KI, and potassium iodate, KIO_3, which remain dissolved in the liquid. Continue the addition of iodine so long as its colour, after a few minutes' warming and stirring, disappears. When the whole of the potassium hydroxide in the solution has been converted into the salts mentioned, the slight excess of iodine remaining in the liquid will colour it, and thus show that this stage of the operation is completed.

$$\underset{\substack{\text{Potassium}\\\text{hydroxide}}}{6KOH} + \underset{\text{Iodine}}{3I_2} = \underset{\substack{\text{Potassium}\\\text{iodide}}}{5KI} + \underset{\substack{\text{Potassium}\\\text{iodate}}}{KIO_3} + \underset{\text{Water}}{3H_2O}$$

Separation of the iodide from the iodate.—Evaporate the solution to dryness. If both salts were required, the resulting mixture might be digested in alcohol, which dissolves the iodide but not the iodate. But the iodide only is needed. Intimately mix the residue, therefore (reserving a grain or two for a subsequent experiment), with excess (about a third of its weight) of charcoal, and gently heat in a test-tube or crucible until slight deflagration ensues.* The crucible may be supported in the flame of a spirit-lamp or Bunsen burner, or placed in a fire or furnace. The iodide remains unaffected; but the iodate loses all its oxygen and is reduced to the state of iodide.

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* If, in the operation of heating potassium iodate with charcoal, excess of the latter be employed, slight incandescence rather than deflagration occurs; if the charcoal be largely in excess, the reduction of the potassium iodate to iodide is effected without visible deflagration or even incandescence.

Deflagration means violent burning, from *flagratus*, burnt (*flagro*, I burn), and *de*, a prefix augmenting the sense of the word to which it may be attached. Paper thrown into a fire simply burns, nitre causes deflagration of the fuel. Detonation (*detono*) is a similarly constructed word, meaning explosion with violent noise.

$$\underset{\substack{\text{Potassium}\\\text{iodate}}}{KIO_3} + \underset{\text{Carbon}}{3C} = \underset{\substack{\text{Potassium}\\\text{iodide}}}{KI} + \underset{\substack{\text{Carbonic}\\\text{oxide}}}{3CO}$$

Treat the mass with a little water, and filter to separate excess of charcoal; a solution of pure potassium iodide results. The latter may be used as a reagent, or it may be evaporated to a small bulk and set aside to crystallize.

This is the officially recognised process for making potassium iodide (*Potassii Iodidum,* B.P.).

Properties.—Potassium iodide crystallizes in small cubical crystals, very soluble in water, less so in alcohol. One part in ten of water forms "Solution of Potassium Iodide," B.P. Exposed to air and sunlight, pure potassium iodide becomes slightly brown, owing, probably, to the combined action of the oxygen, water vapour, and carbonic anhydride of the atmosphere.

The addition of charcoal in the above process is simply to facilitate the removal of the oxygen from the potassium iodate. Potassium iodate, KIO_3, is analogous in composition to potassium chlorate, $KClO_3$, which has already been stated to be more generally used than any other salt for the actual preparation of oxygen gas itself, and the removal of its oxygen may be accomplished by heating the residue without charcoal. In this case the liberated oxygen can be detected by inserting a glowing strip of wood into the mouth of the test-tube in which the mixture of iodide and iodate is being heated. The charcoal, however, removes the oxygen more quickly and at a lower temperature, and thus economizes both time and heat.

Detection of iodate in iodide.—Potassium iodate remaining as an impurity in potassium iodide, may be detected by adding to a solution of the latter salt some weak acid (say, tartaric), shaking, and then adding starch mucilage; blue "iodide of starch" (*see* Starch) is formed if a trace of iodate be present, but not otherwise. By the interaction of the added acid and the potassium iodate, iodic acid, HIO_3, is produced; and by interaction of the added acid and the potassium iodide, hydriodic acid, HI, is produced; neither of these alone attacks starch, but by their mutual interaction they yield free iodine, which then forms the blue colour by its action on the starch. This experiment should be tried on a grain or two of pure iodide and on the impure iodide reserved from the previous experiment.

Potassium iodide containing iodate would obviously yield free iodine, which is excessively corrosive, on the salts coming into contact with the acids of the stomach.

$$HIO_3 + 5HI = 3H_2O + 3I_2$$

Note on Nomenclature.—The final syllable *ide* in the name potassium iodide, indicates that the *element* iodine is combined with potassium. An iod*ate*, as already explained, is a salt containing the characteristic radical of iod*ic* acid and of all other iodates. Inorganic salts whose names end in *ide*, are derived from acids which do not contain oxygen. Acids with complex radicals, the latter usually containing oxygen, give rise to salts with names ending in *ate* (*see* p. 75) or *ite*. An inorganic salt whose name ends in *ate* contains the radical of an acid whose name ends in *ic*; a salt whose name ends in *ite* contains the radical of an acid whose name ends in *ous*; an inorganic salt whose name ends in *ide* contains an element for its acid radical. Thus an inorganic sulph*ide* consists of a metallic radical combined with sulphur only, while a sulph*ite* and a sulph*ate* are compounds of metallic radicals with the sulphur*ous* and the sulphur*ic* acid radicals respectively, and so on with other inorganic "ides," "ites," or "ates."

Potassium Bromide (*Potassii Bromidum*, B.P.).—This salt is analogous in composition with potassium iodide, and is made in the same way, bromine being substituted for iodine. The formula of bromic acid is $HBrO_3$. It will be noticed that the following equations are similar in character to those showing the preparation of potassium iodide:—

$$\underset{\substack{\text{Potassium}\\\text{hydroxide}}}{6KOH} + \underset{\text{Bromine}}{3Br_2} = \underset{\substack{\text{Potassium}\\\text{bromide}}}{5KBr} + \underset{\substack{\text{Potassium}\\\text{bromate}}}{KBrO_3} + \underset{\text{Water}}{3H_2O}$$

$$\underset{\substack{\text{Potassium}\\\text{bromate}}}{KBrO_3} + \underset{\text{Carbon}}{3C} = \underset{\substack{\text{Potassium}\\\text{bromide}}}{KBr} + \underset{\substack{\text{Carbonic}\\\text{oxide}}}{3CO}$$

Potassium Manganate and Permanganate

Experiment 8.—Place a fragment of solid potassium hydroxide, KOH, with about the same quantity of potassium chlorate, $KClO_3$, and of black manganese oxide, MnO_2, on a piece of platinum foil.* Hold the foil, by means of a small pair of forceps or tongs, in the flame of a blowpipe for a few minutes until the fused mixture has become dark green—apparently black. This colour is that of *potassium manganate*, K_2MnO_4.

$$\underset{\substack{\text{Potassium}\\ \text{hydroxide}}}{6KOH} + \underset{\substack{\text{Potassium}\\ \text{chlorate}}}{KClO_3} + \underset{\substack{\text{Black man-}\\ \text{ganese oxide}}}{3MnO_2} = \underset{\substack{\text{Potassium}\\ \text{manganate}}}{3K_2MnO_4} + \underset{\substack{\text{Potassium}\\ \text{chloride}}}{KCl} + \underset{\text{Water}}{3H_2O}$$

Experiment 9.—Potassium Permanganate (*Potassii Permanganas*, B.P.), $KMnO_4$. Boil the potassium manganate from Experiment 8 in water for a short time. Potassium permanganate is formed, and yields a purple solution.

$$\underset{\substack{\text{Potassium}\\ \text{manganate}}}{3K_2MnO_4} + \underset{\text{Water}}{2H_2O} = \underset{\substack{\text{Potassium}\\ \text{permanganate}}}{2KMnO_4} + \underset{\substack{\text{Potassium}\\ \text{hydroxide}}}{4KOH} + \underset{\substack{\text{Black man-}\\ \text{ganese oxide}}}{MnO_2}$$

On the large scale, the potassium hydroxide set free in the reaction is neutralized by sulphuric or, better, by carbonic acid, and the solution is evaporated to the crystallizing point. Manganate may also be changed into permanganate by treatment with chlorine.

$$2K_2MnO_4 + Cl_2 = 2KCl + 2KMnO_4$$

Solutions of potassium manganate (green) or permanganate (purple) and the analogous sodium compounds so readily yield their oxygen to organic matter that they are used on the large scale as disinfectants.

Experiments dealing with the remaining official potassium compounds (namely, potassium bichromate, arsenite, chlorate, cyanide, ferrocyanide, and ferricyanide), are deferred at present.

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* The foil may be 1 in. broad by 2 in. long. No ordinary flame will melt the platinum, fused caustic alkalies only slowly corrode it, and very few other chemical substances affect it at all; hence the same piece may be used in experiments over and over again. Many metals form a fusible alloy with platinum, and phosphorus and arsenious sulphide rapidly attack it; hence such substances, as well as mixtures likely to yield them, should be heated in porcelain vessels.

Crystallization.—This operation will have been performed several times in the course of the foregoing experiments. Obviously it offers a mode of separating soluble crystallizable substances from soluble *amorphous* (*α, a,* without; *μορφή, morphe,* shape) substances; also of separating from each other, by *fractional crystallization,* substances of varying degrees of solubility.

Analytical Reactions of Potassium Salts.

Note.—Each reaction should be expressed in the form of an equation or diagram by the student in his note-book.

1. To a solution of any salt of potassium (chloride,[*] for example) add a few drops of hydrochloric acid and of a solution of platinic chloride in hydrochloric acid (really chloroplatinic acid, H_2PtCl_6),[†] and stir the mixture with a glass rod; a yellow granular or slightly crystalline precipitate[‡] slowly forms. This precipitate consists of potassium chloroplatinate, K_2PtCl_6; it is very sparingly soluble in water, and practically insoluble in alcohol.

Memoranda.—When the precipitate forms very slowly, it is sometimes of an orange-yellow tint. If potassium iodide happen to be the potassium salt under examination, compounds of iodine and platinum will be formed, giving a red colour to the solution, and a larger quantity of the *precipitant* (that is the precipitating agent) will be required.

Educational Note.—The thoughtful student will not confuse *the test* with the *chemistry of the test.* The test itself appeals to the senses; commonly to the eye, sometimes to the nose, occasionally to the ear. A person may be able to apply a test, and yet never know anything of the chemistry of the test.

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[*] A few fragments of potassium carbonate, two or three drops of hydrochloric acid, and a small quantity of water, give a solution of potassium chloride at once, $K_2CO_3 + 2HCl = 2KCl + H_2O + CO_2$.

[†] Experiments with reagents containing platinum or other expensive metals are economically performed in watch-glasses, drops of the liquids being operated on.

[‡] By *precipitation* (from *præcipitare,* to throw down suddenly) is simply meant the formation of particles of solid in a liquid, no matter whether the solid, the *precipitate,* subsides or floats, and no matter whether the operation be partial or complete.

2. *Carnot's test for potassium.*—Mix one drop of a solution of bismuth nitrate with one drop of a solution of sodium thiosulphate, and add to the mixture 10 c.c. or so of absolute alcohol. To the reagent so prepared, add one or two drops of a solution of a potassium salt. A yellow precipitate of potassium bismuth thiosulphate, $K_3Bi(S_2O_3)_3$, is produced either immediately or very nearly so (depending upon the concentration of the solution of the potassium salt added). If produced in large quantity, the precipitate settles down in a bulky flocculent form. Although insoluble in nearly absolute alcohol, the precipitate is readily soluble in water and in dilute alcohol, hence it is essential that no considerable quantity of water should be present. Very dilute solutions of potassium salts should be concentrated by evaporation before employing them for this reaction.

Acid Potassium Tartrate. Potassium Hydrogen Tartrate. Potassium Bitartrate

3. To a solution of any salt of potassium add excess of a saturated solution of acid sodium tartrate (sodium hydrogen tartrate), $NaHC_4H_4O_6$, and shake or well stir the mixture; a white granular precipitate of acid potassium tartrate (potassium hydrogen tartrate), $KHC_4H_4O_6$, will be formed. If the solution of potassium salt employed is alkaline (solution of potassium carbonate, for example), care must be taken to add the sodium hydrogen tartrate solution until the liquid, after thorough mixing, is acid to test paper, otherwise the precipitate will not be formed. (Solution of sodium hydrogen tartrate possesses a strongly acid reaction.) Test paper, *see* p. 101.

Note.—By "excess" of any test-liquid (such as the "solution of acid sodium tartrate" just mentioned) an excessively large quantity is not to be understood, but merely such a quantity of the reagent as is more than sufficient (however little more) to convert the whole weight of the compound attacked into the compound to be produced. Thus, in the present case, enough sodium hydrogen tartrate must be added to convert the whole of the potassium salt operated on into acid potassium tartrate. What the weight of salt operated on was, must be roughly estimated mentally by the operator. It is not necessary in analytical operations to know the exact weights of salts employed. The analyst must use his judgment, founded on his knowledge of the reaction (as shown by an equation), and of the molecular weights of the substances employed in the reaction, as well as by the rough estimate of the amount of material on which he is experimenting.

Limits of the test.—Acid potassium tartrate is soluble in 200 parts of cold and in 6 parts of boiling water. Hence, in applying the acid sodium tartrate test for potassium, the solutions must not be hot. Even if cold, no precipitate will be obtained if the solutions are very dilute. This test, therefore, is of far less value than either of the two already mentioned. Acid potassium tartrate is less soluble in dilute alcohol than in water, so that the addition of alcohol renders the reaction somewhat more delicate.

Cream of Tartar. — The precipitate is *Potassii Tartras Acidus*, B.P., long known as Cream of Tartar (although the official preparation is not formed in the above manner).

4. The *flame-test.*—Dip the looped end of a platinum wire into a solution of a potassium salt, and introduce the loop into the lower part of the flame of a spirit-lamp or Bunsen burner. A light violet or lavender tint will be communicated to the flame, an effect highly characteristic of salts of potassium.

Potassium salts are not readily volatile. Place a fragment of carbonate, nitrate, or other potassium salt, on a piece of platinum foil, and heat the latter in the flame of a lamp; the salt may fuse to a transparent liquid and flow over the foil; water also, if present, will escape as steam, and black carbon be set free, if the salt happen to be a tartrate, citrate, etc.; but the potassium compound itself will not be vaporized to any appreciable extent unless exposed to an exceedingly high temperature. This is a valuable negative property, as will be evident when the analytical reactions of ammonium come under notice.

5. A solution of sodium cobaltic nitrite * is a very delicate test for potassium, in the absence of ammonium, potassium salts forming with it a yellow precipitate of potassium cobaltic nitrite (Fischer's salt), $K_3Co(NO_2)_6$, even in extremely dilute solutions.

QUESTIONS AND EXERCISES

Name the sources of potassium.—Give the source, formula, and characters of Potassium Carbonate.—What is the systematic name of Caustic Potash?—State the chemical formula of Caustic Potash.—Construct an equation representing the reaction between potassium carbonate and slaked lime.—Define a *hydroxide*.—What group of atoms is characteristic of all carbonates?—How is "Sulphurated Potash" made, and of what salts is it a mixture?—What is the formula for the acid radical of all acetates?—Draw a diagram showing the formation of Potassium Acetate.—Give a process for the conversion of carbonates into other salts.—What is the difference between Potassium Carbonate and Bicarbonate? How is the latter prepared?—What is the relation between salts whose specific names end in the syllable "*ate*," and acids ending in "*ic*"?—Construct diagrams or equations representing the formation of Potassium Tartrate from Acid Tartrate, and Potassium Citrate from Carbonate.—Distinguish between a normal and an acid salt.—How is Potassium Iodide made? Illustrate the process either by diagrams or equations.—Calculate how much potassium iodide is producible from 1000 grains of iodine. *Ans.*, 1308·5 grains.—Give a method for the detection of iodate in potassium iodide. Explain the reaction.—What is the signification of the termination "*ide*" in chemical nomenclature?—State the relations between sulphides, sulphites, and sulphates.—Mention the chemical relation of Potassium Bromide to Potassium Iodide.—Describe the formation of Potassium Permanganate, giving equations or diagrams.—How do manganates and permanganates act as disinfectants?—Enumerate the tests for potassium, explaining by diagrams or equations the various reactions which occur.

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* *Preparation of Sodium Cobaltic Nitrite.*—Slowly add five fluid ounces of a sixty per cent. solution of sodium nitrite, $NaNO_2$, to a solution of 1½ ounce of cobaltous nitrate, $Co(NO_3)_2$, in 3 ounces of water; allow to stand till evolution of gas ceases, filter, and precipitate the sodium cobaltic nitrite, $Na_3Co(NO_2)_6$, from the filtrate by the addition of alcohol.

SODIUM: Na. Atomic weight, 22·88

Occurrence, etc.—Most of the sodium salts met with in pharmacy are obtained directly from sodium carbonate, which is now manufactured on an enormous scale from sodium chloride (common salt, sea-salt, bay-salt, or rock-salt), the most abundant of the sodium salts. When pure, common salt (*Sodii Chloridum,* B.P.) occurs "in small white crystalline grains or transparent cubic crystals, free from moisture"; the best varieties commonly contain a little magnesium chloride, and sometimes other impurities. Besides the direct and indirect use in medicine of sodium carbonate, or "carbonate of soda" as it is commonly called, this substance is largely used for household cleansing purposes, under the name of "washing soda," and in the manufacture of soap. Sodium nitrate also occurs in nature, but is valuable as a nitrate rather than as a sodium salt. Sodium, in the form of one or other of its compounds, is a constituent of about forty chemical or galenical preparations of the British Pharmacopœia.

Sodium (*Sodium,* B.P.) is prepared by a process similar to that for potassium, but at a somewhat lower temperature. Castner obtained it comparatively cheaply by distillation from a mixture of sodium hydroxide, carbon, and iron, contained in steel vessels. The modern Castner process for preparing sodium, by which large quantities are now obtained, consists in electrolysing fused sodium hydroxide. The metal has a bright metallic lustre when freshly cut, but is rapidly attacked by atmospheric oxygen, moisture, and carbonic anhydride, and eventually becomes coated with sodium carbonate. Thrown upon the surface of water, sodium displaces hydrogen from the water, yielding solution of sodium hydroxide; but unless the sodium is confined to one spot, by placing it on a small floating piece of filter-paper, the action is not sufficiently intense to cause ignition of the escaping hydrogen. When the latter does ignite, it burns with a yellow flame, due to the presence of a small quantity of sodium vapour.

$$\underset{\text{Sodium}}{2\text{Na}} + \underset{\text{Water}}{2\text{H}_2\text{O}} = \underset{\text{Hydrogen}}{\text{H}_2} + \underset{\text{Sodium hydroxide}}{2\text{NaOH}}$$

Sodium similarly attacks alcohol, yielding sodium ethylate (*see* Index). It may be kept beneath the surface of mineral naphtha, or in sealed tins out of contact with air. It crystallizes in octahedra.

Sodium Hydroxide. Caustic Soda

The formation of solution of sodium hydroxide, or caustic soda, NaOH, is effected by a process resembling that employed for making solution of potassium hydroxide, already described.

$$\underset{\substack{\text{Sodium}\\\text{carbonate}}}{Na_2CO_3} + \underset{\substack{\text{Calcium}\\\text{hydroxide}}}{Ca(OH)_2} = \underset{\substack{\text{Sodium}\\\text{hydroxide}}}{2NaOH} + \underset{\substack{\text{Calcium}\\\text{carbonate}}}{CaCO_3}$$

The remarks made concerning the general properties of solution of potassium hydroxide apply to this solution also.

In the Castner process, which is in operation on the manufacturing scale, sodium hydroxide is obtained as a product of the electrolysis of a solution of sodium chloride. The chlorine simultaneously liberated at the anode as another product of this electrolysis, is used in the manufacture of bleaching powder (*see* p. 125).

The interaction of sulphur and sodium carbonate at a high temperature resembles that of sulphur and potassium carbonate; but as the product is not used in medicine the experiment may be omitted. It is mentioned here to draw attention to the general resemblance of the potassium salts to those of sodium.

Sodium Acetate

Experiment 1.—Add sodium carbonate (in powder or, better, in fragments) to some moderately concentrated acetic acid in an evaporating-basin as long as effervescence occurs, and then boil off some of the water. When the fluid is cold, crystals of "Sodium Acetate," B.P., $NaC_2H_3O_2, 3H_2O$ (*Sodii Acetas,* U.S.P.), will be deposited. A ten per cent. solution in distilled water forms "Solution of Sodium Acetate," B.P.

$$\underset{\substack{\text{Sodium}\\\text{carbonate}}}{Na_2CO_3} + \underset{\substack{\text{Acetic}\\\text{acid}}}{2HC_2H_3O_2} = \underset{\substack{\text{Sodium}\\\text{acetate}}}{2NaC_2H_3O_2} + \underset{\text{Water}}{H_2O} + \underset{\substack{\text{Carbonic}\\\text{anhydride}}}{CO_2}$$

Sodium acetate effloresces (*see* p. 90) in dry air, and loses all its water of crystallization when gently heated. It withstands a temperature of 270° to 280° F. (about 132° to 138° C.) without decomposition, but above 300° F. (about 149° C.) it rapidly chars. Its extended formula is $CH_3{\cdot}COONa, 3H_2O$.

Sodium Hydrogen Carbonate. Sodium Bicarbonate

The action of carbonic anhydride and water on sodium carbonate, Na_2CO_3, resembles that on potassium carbonate, but is carried out in a different manner. The result is sodium bicarbonate, $NaHCO_3$ (*Sodii Bicarbonas*, B.P.).

$$\underset{\text{Sodium carbonate}}{Na_2CO_3} + \underset{\text{Water}}{H_2O} + \underset{\text{Carbonic anhydride}}{CO_2} = \underset{\text{Sodium bicarbonate}}{2NaHCO_3}$$

Experiment 2.—Heat crystals of sodium carbonate in a porcelain crucible until no more steam escapes. Rub the product, in a mortar, with two-thirds of its weight of the crystallized salt which has not been deprived of its water, and place the powder in a test-tube or small bottle into which carbonic anhydride may be conveyed by a tube passing through a cork and terminating at the bottom of the vessel. To generate the carbonic anhydride, fill a test-tube having a small hole in the bottom (or a piece of wide glass tubing, the lower end of which is plugged by a grooved cork), with fragments of marble, insert a cork and delivery-tube, and connect the latter, by means of a piece of indiarubber tubing, with the tube leading into the vessel containing the sodium carbonate. Now plunge the tube which contains the marble into a test-glass, or other vessel, containing a mixture of one part of hydrochloric acid and two parts of water, and loosen the cork of the sodium carbonate tube until carbonic anhydride, generated from the marble, may be considered to have displaced all the air of this tube; then replace the cork tightly and set the apparatus aside. As the gas is absorbed by the sodium carbonate, hydrochloric acid rises into the tube containing the marble, and generates fresh

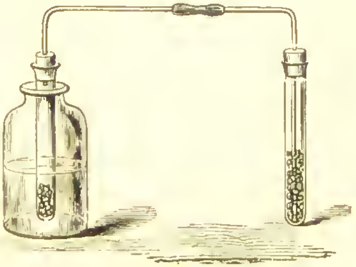

Fig. 19.—Preparation of Sodium Bicarbonate.

gas, which, in its turn, drives back the acid liquid, and thus prevents the production of any more gas until further absorption has occurred. When the salt is wholly converted into bicarbonate, $NaHCO_3$, it will be found to have become damp through the liberation of some water from the crystallized carbonate, $Na_2CO_3, 10H_2O$. (It would be inconveniently moist, even semi-fluid, if a part of the carbonate had not previously been rendered anhydrous.) On the large scale, the resulting bicarbonate may be freed from any carbonate or traces of other salts, by adding half its bulk of cold distilled water, setting aside for about half an hour, shaking occasionally, draining the undissolved portion, and drying it by exposure to the air on filter-paper.

This arrangement of apparatus for the preparation of sodium bicarbonate may be adopted for potassium bicarbonate, one part of potassium carbonate dissolved in two and a half parts of water being subjected to the action of the gas, and not the solid carbonate, as in the case of the sodium salt.

The sodium carbonate may be placed, not in a test-tube or bottle, but in a vertical tube, the bottom of which is loosely closed by a grooved cork. Any water of crystallization that is set free then runs off into a vessel placed beneath, and takes with it impurities (chlorides, sulphates, etc.) that may have been present in the original salt.

The Ammonia Process.

Sodium bicarbonate is now prepared on the manufacturing scale by treating a concentrated solution of sodium chloride, which has been saturated with ammonia, with carbonic anhydride under a pressure somewhat greater than that of the atmosphere. Sodium bicarbonate, which is sparingly soluble, is slowly precipitated. The ammonia and the carbonic anhydride may be considered to behave in the reaction as ammonium bicarbonate.

$$\underset{\substack{\text{Ammonium}\\\text{bicarbonate}}}{NH_4HCO_3} + \underset{\substack{\text{Sodium}\\\text{chloride}}}{NaCl} = \underset{\substack{\text{Sodium}\\\text{bicarbonate}}}{NaHCO_3} + \underset{\substack{\text{Ammonium}\\\text{chloride}}}{NH_4Cl}$$

Ammonia is recovered from the resulting ammonium chloride, and is again used for saturating solution of sodium chloride which is to be employed in subsequent operations for preparing further quantities of sodium bicarbonate. Sodium carbonate, Na_2CO_3, $10H_2O$ (*Sodii Carbonas*, B.P.), is made by heating the bicarbonate thus obtained, and crystallizing from aqueous solution, the carbonic anhydride liberated during the heating process being also utilised in the preparation of further quantities of sodium bicarbonate.

$$\underset{\substack{\text{Sodium}\\\text{bicarbonate}}}{2NaHCO_3} = \underset{\substack{\text{Sodium}\\\text{carbonate}}}{Na_2CO_3} + \underset{\text{Water}}{H_2O} + \underset{\substack{\text{Carbonic}\\\text{anhydride}}}{CO_2}$$

Sodium bicarbonate may be medicinally administered in the form of lozenge (*Trochiscus Sodii Bicarbonatis*, B.P.).

Sodium Carbonate

Sodium carbonate may be obtained by heating the sodium bicarbonate produced by the ammonia process described above, the resulting salt being anhydrous. The hydrous sodium carbonate of the Pharmacopœia is obtained by dissolving the anhydrous salt in water and crystallizing.

Sodium carbonate is also prepared on the large scale by the Leblanc process. Sodium chloride is first converted into sulphate (salt-cake) by heating it with sulphuric acid:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

The sulphate is then roasted with limestone and small coal, sodium carbonate and calcium sulphide being formed:

$$Na_2SO_4 + 2C + CaCO_3 = CaS + Na_2CO_3 + 2CO_2$$

The resulting mass (black-ash) is lixiviated. (*Lixivia,* from *lix,* lye—water impregnated with alkaline salts; hence *lixiviation,* the operation of washing a mixture with a view to dissolve out soluble constituents. If relatively small quantities of solvents be employed, the solution by lixiviation will be more or less *fractional,* substances of varying solubility being thus more or less separated from each other.) The sodium carbonate dissolves, the calcium sulphide remaining insoluble. The solution is evaporated to dryness, and yields crude sodium carbonate. This is roasted with a small quantity of sawdust, to reconvert into carbonate any caustic soda produced by the action of lime on the sodium carbonate. The product is *soda-ash.* Dissolved in water and crystallized, it constitutes ordinary "washing-soda": recrystallized (and sometimes ground) it forms the official sodium carbonate, $Na_2CO_3, 10H_2O$ (*Sodii Carbonas*, B.P.).

In the Hargreaves-Bird electrolytic process for the manufacture of sodium carbonate, the sodium hydroxide obtained by the electrolysis of a solution of sodium chloride is treated with a mixture of steam and furnace gases (the latter furnishing carbonic anhydride), whereby a solution is obtained which only requires evaporation to a small extent in order to yield crystals of sodium carbonate on cooling.

A *crystal* of sodium carbonate is sodium carbonate plus "water of crystallization"; on heating it, part or the whole of the water is evolved. Exsiccated sodium carbonate (*Sodii Carbonas Exsiccatus*, B.P.) is obtained by heating crystallized sodium carbonate until it loses nearly 63 per cent. of its weight.

$$\underset{\substack{\text{Crystallized sodium}\\\text{carbonate (284·11)}}}{\mathrm{Na_2CO_3,\ 10H_2O}} \quad - \quad \underset{\substack{\text{Water}\\\text{(178·8)}}}{\mathrm{10H_2O}} \quad = \quad \underset{\substack{\text{Dried sodium}\\\text{carbonate (105·31)}}}{\mathrm{Na_2CO_3}}$$

Water of Crystallization.—Anhydrous and Hydrous Salts. Efflorescence. Anhydrides.—A number of salts, when crystallizing from aqueous solution, take up water to a greater or less extent from the solution. Sometimes the same salt is capable of combining with water in two or more different proportions. Salts which do not combine with water in this way are often called *anhydrous* (from *ἀ, a*, without, and *ὕδωρ, hudōr*, water) as distinguished from those which do, and are, in consequence, called *hydrous* salts. The water so taken up by certain salts in crystallizing is generally called *water of crystallization*. Many hydrous salts, when simply exposed to moderately dry air at ordinary temperatures, lose water and crumble to a fine powder. This process is known as *efflorescence* (*efflorescens*, blossoming forth, in allusion to the appearance of the product). The water of crystallization is usually (although not in all cases completely) expelled from a hydrous salt by heating it to a temperature of 100° to 150° C. In the chemical formulæ of salts with water of crystallization, the symbols representing water are usually separated by a comma from those representing the salts. The crystals of sodium acetate (Experiment 1, p. 86) are represented by the formula $NaC_2H_3O_2, 3H_2O$, and those of sodium carbonate by the formula $Na_2CO_3, 10H_2O$. It is possible, however, that this so-called water of crystallization is in a more intimate state of combination than is indicated by such formulæ as those just given. *Anhydrides* form a distinct class of chemical substances derived from or related to acids: in short, they may be regarded as acids from which the elements of water have been removed, the essential chemical properties of the acids being thereby greatly altered.

Deliquescence.—Sodium carbonate and potassium carbonate, chemically closely allied, differ physically. Potassium carbonate quickly absorbs moisture from the air and becomes damp, wet, and finally a solution—it is *deliquescent* (*deliquescens*, melting away). Sodium carbonate, on the other hand, is efflorescent, and yields water of crystallization to the air, the crystals becoming white, opaque, and pulverulent.

Sodium Potassium Tartrate

Experiment 3.—To some hot concentrated solution of sodium carbonate (about three parts), in a test-tube or larger vessel, add acid potassium tartrate (about four parts) till no more effervescence occurs; when the solution is cold, crystals of sodium potassium tartrate, $KNaC_4H_4O_6 \, 4H_2O$, (*Soda Tartarata*, B.P.; *Potassii et Sodii Tartras*, U.S.P.), long known as *Rochelle Salt*, will be deposited. The crystals are large rhombic prisms.

$$\underset{\text{Sodium carbonate}}{\mathrm{Na_2CO_3}} + \underset{\text{Acid potassium tartrate}}{\mathrm{2KHC_4H_4O_6}} = \underset{\text{Sodium potassium tartrate}}{\mathrm{2KNaC_4H_4O_6}} + \underset{\text{Water}}{\mathrm{H_2O}} + \underset{\text{Carbonic anhydride}}{\mathrm{CO_2}}$$

Sodium Hypochlorite

Experiment 4.—Triturate in a mortar 2 parts of chlorinated lime with a solution of 3 parts of sodium carbonate in 20 of water, and filter. The filtrate is the official solution of chlorinated soda (*Liquor Sodæ Chlorinatæ*, B.P.).

$$\underset{\text{Chlorinated lime}}{\mathrm{[Ca(ClO)_2 + CaCl_2]}} + \underset{\text{Sodium carbonate}}{\mathrm{2Na_2CO_3}} = \underset{\text{Chlorinated soda}}{\mathrm{2[NaClO + NaCl]}} + \underset{\text{Calcium carbonate}}{\mathrm{2CaCO_3}}$$

This solution is an old and very useful disinfectant, formerly known as *Labarraque's* liquor and *Eau de Javelle*. It contains about $2\frac{1}{2}$ per cent. of available chlorine.

Sodium Iodide and Sodium Bromide

These salts, NaI and NaBr (*Sodii Iodidum*, B.P., and *Sodii Bromidum*, B.P.), are analogous in composition with potassium iodide and bromide, and are prepared by a similar method, sodium hydroxide being used in place of potassium hydroxide. Sodium bromide, however, must be crystallized from warm solutions, otherwise rhombic prisms containing water, $NaBr,2H_2O$, will be deposited.

Other Sodium Compounds

Experiments dealing with the chemistry of the remaining important sodium compounds (namely, nitrate, sulphate, thiosulphate, borate, arsenate, valerianate, and ethylate) are deferred for the present.

Sodium Phosphate.—The preparation and composition of this salt will be most usefully studied after bone-ash has been described. Bone-ash is impure calcium phosphate, and is the starting point for the preparation of most other phosphates and for phosphorus itself.

The official Effervescent Sodium Citro-Tartrate (*Sodii Citro-tartras Effervescens*, B.P.) is a mixture of sodium bicarbonate (17 parts), citric acid (6), tartaric acid (9), and sugar (5), which has been heated to 200° or 220° F. (about 93° to 104° C.) and manipulated so as to assume a granular character. When required for medicinal use, an appropriate quantity of the mixture is placed in water ; escape of carbonic anhydride at once occurs, and an effervescing liquid results. This substance may be regarded as the official representative of the popular Effervescing Citrate of Magnesia, so-called, which will be further noticed in connection with the salts of magnesium.

Sodii Phosphas Effervescens, B.P., and *Sodii Sulphas Effervescens*, B.P., are the respective *anhydrous* salts, mixed with sodium bicarbonate and tartaric and citric acids.

Soda Powders (*Pulveres Effervescentes*, U.S.P., 1870).—Formed of 30 grains of sodium bicarbonate and 25 of tartaric acid, wrapped separately in papers of different colours. When mixed with water, carbonic anhydride escapes, and sodium tartrate, $Na_2C_4H_4O_6$, results, a little sodium bicarbonate also remaining.

Sodium peroxide, Na_2O_2, a compound now manufactured on a large scale, is used as a bleaching agent.

Analogies of Sodium and Potassium salts.—Other reactions similar to those given under potassium might be mentioned here, and the preparation of sodium citrate, iodate, bromate, chlorate, manganate, permanganate, and many other salts be described. But enough has been stated to show how sodium is chemically analogous to potassium. Such analogies will frequently present themselves.

Substitution of Potassium and Sodium salts for each other.—Sodium salts being cheaper than potassium salts, the former may sometimes be economically substituted. That one is employed rather than the other, is often merely a result due to accident or fashion. But it must be borne in mind that in some cases a potassium salt crystallizes more readily than its sodium analogue, or that a sodium salt is unchanged by exposure to the air when the corresponding potassium salt has a tendency to absorb moisture; or one may be more soluble than the other, or the two may have different medicinal effects. For these or similar reasons, a potassium salt has come to be used in medicine or trade instead of the corresponding sodium salt, and *vice versâ*. When a salt is employed as a source of a particular acid radical, the least expensive salt of that radical is nearly always selected.

Analytical Reactions of Sodium Salts.

1. *The chief analytical reaction* for sodium is *the flame-test.* When brought into contact with a Bunsen flame in the manner described under Potassium (page 83), an intensely yellow colour is communicated to the flame by any sodium salt. This is highly characteristic—indeed, almost too delicate a test; for if the end of the wire be touched by the fingers, enough sodium salt (which is contained in the moisture of the hand) adheres to the wire to communicate a very distinct sodium reaction to the flame. These statements should be experimentally verified, sodium chloride, sulphate, or other salt being employed.

2. Sodium salts, like those of potassium, are not volatile. Prove this fact by the means described where the effect of heat on potassium salts is referred to (p. 83).

QUESTIONS AND EXERCISES

Explain the action of sodium on water. What colours do sodium and potassium respectively communicate to flame?—How much sodium bicarbonate can be obtained from 2240 pounds of crystallized carbonate? *Ans.*, 1315·5 lbs.—Sodium Acetate: give formula and preparation, with equation.—Give a diagram showing the formation of Sodium Bicarbonate.—Why is a mixture of dried and undried sodium carbonate employed in the preparation of the bicarbonate?—State the difference between anhydrous and crystallized sodium carbonate.—Define the terms *anhydrous*, *hydrous*, *anhydride*.—What do you understand by *water of crystallization?*—What is the systematic name of *Soda Tartarata*, B.P., and how is the salt prepared?—What is the relation of Rochelle salt to cream of tartar and tartaric acid?—Give the mode of preparation of the official Solution of Chlorinated Soda, representing the process by a diagram.—How is the effervescing Sodium Citro-tartrate prepared?—Define *deliquescence*, *efflorescence*, and *lixiviation*.—How are sodium salts distinguished from those of potassium?

AMMONIUM

Radical of the ammonium compounds, NH_4

The elements nitrogen and hydrogen, in the proportion of one atom of the former to four of the latter (NH_4), are present in all the ammonium compounds about to be studied, playing the part of metallic radical just as potassium (K) and sodium (Na) do in the potassium and sodium compounds. The group NH_4 is univalent like potassium and sodium, and the ammonium compounds closely resemble those of potassium and sodium. Ammonium is said to have been isolated, by Weyl, as an unstable dark-blue liquid, possessing a metallic lustre.

Source.—The source of nearly all the ammonium salts met with in commerce is the ammonia gas, NH_3, produced during the distillation of all kinds of coal in the manufacture of ordinary illuminating gas and of coke. This ammonia is no doubt derived from the nitrogen of the plants from which the coal has been produced. It is obtained as a by-product in the distillation of shale for the production of paraffin oil, and is also recovered from the furnace gases of iron-works. It is possible, however, to produce ammonia from its elements. Thus when electric sparks are passed through a mixture of nitrogen and hydrogen, or when a similar mixture is passed over spongy platinum, some ammonia is produced. According to Rickman and Thompson, coal-dust, air, and vapour of water, all at a red heat, yield ammonia. Salt added to the mixture prevents the combustion of the ammonia formed, and ammonium chloride sublimes.

Ammonium Chloride.—The ammonia liberated from the "ammoniacal liquor" of the gas-works by heat and by the concurrent action of slaked lime on the ammonium hydrosulphide, carbonate, and other salts present, when passed into hydrochloric acid, yields crude *ammonium chloride* (sal-ammoniac), $NH_3 + HCl = NH_4Cl$; and from this salt, purified, the others used in pharmacy are directly or indirectly made. Ammonium Chloride (*Ammonii Chloridum*, B.P.) occurs in colourless inodorous minute crystals, or in translucent fibrous masses, tough, and difficult to powder, soluble in water (1 in 10 is the "Solution of Ammonium Chloride," B.P.) and in alcohol (90 per cent.).

Commercial ammonium chloride generally contains slight traces of iron oxychloride, tarry matter, and possibly compound ammonium chlorides (*see* "Artificial Alkaloids" in Index).

Ammonium Sulphate, $(NH_4)_2SO_4$, is formed when the ammonia of the ammoniacal liquor is neutralized with sulphuric acid. It is largely used as a constituent of artificial manure; and when purified by recrystallization, is employed in pharmacy for producing the double ammonium and ferric sulphate (iron alum).

Volcanic Ammonia.—A very pure form of ammonia is that met with in volcanic districts, and obtained as a by-product in the manufacture of borax. Crude boric acid as imported contains 5 to 10 per cent. of ammonium salts, either sulphate or that salt united with magnesium, sodium, or manganese sulphates, forming so-called *double salts* (*Howard*).

Ammonium Amalgam

Experiment 1.—To forty or fifty grains of mercury in a *dry* test-tube, add one or two small pieces of sodium (freed from adhering naphtha by gentle pressure with a piece of filter-paper), and gently warm the tube, when the metals will unite with evolution of heat to form sodium amalgam. To this amalgam, when cold, add some fragments of ammonium chloride and a concentrated solution of the same salt. The sodium amalgam rapidly swells up and may even overflow the tube. The light spongy mass produced is the so-called ammonium amalgam, and the reaction is usually adduced as evidence of the existence of ammonium. The sodium of the amalgam unites with the chlorine of the ammonium chloride, while the ammonium is supposed to form an amalgam with the mercury. At ordinary temperatures the amalgam rapidly gives off hydrogen and ammonia gases; this decomposition is nearly complete after some minutes, and mercury remains, together with solution of sodium chloride.

Ammonia. Ammonium Hydroxide

Experiment 2.—Heat a few grains of ammonium chloride with about an equal weight of calcium hydroxide (slaked lime) moistened with a little water in a test-tube; ammonia gas is given off, and may be recognised by its pungent odour. It is very soluble in water. By means of a cork and delivery-tube, fitted as described for the preparation of oxygen and of hydrogen, pass some of the ammonia into another test-tube containing a little water. The end of the delivery-tube should only just dip beneath the surface of the water (or, possibly, all the water might rush back into the generating-tube, on account of the water greedily absorbing the ammonia gas). A solution of ammonia will thus be formed.

$$\underset{\substack{\text{Ammonium}\\\text{chloride}}}{2NH_4Cl} + \underset{\substack{\text{Calcium}\\\text{hydroxide}}}{Ca(OH)_2} = \underset{\substack{\text{Calcium}\\\text{chloride}}}{CaCl_2} + \underset{\text{Water}}{2H_2O} + \underset{\text{Ammonia}}{2NH_3}$$

A molecule of ammonia is composed of one atom of nitrogen with three atoms of hydrogen; its formula is NH_3. Two volumes of the gas contain one volume of nitrogen combined with three volumes of hydrogen. Its constituents have, therefore, in combining suffered condensation to one-half of their original bulk.

The solution obtained by dissolving ammonia in water is believed to contain ammonium hydroxide, NH_4OH, the analogue of potassium hydroxide, KOH, or sodium hydroxide, NaOH. The chemical grounds for this belief are the observed analogies of the well-known ammonium salts with those of potassium and sodium, the similarity of action of solutions of caustic potash, caustic soda, and ammonia on salts of most metals, and the asserted existence of crystals of an analogous sulphur salt (NH_4SH). The formation of ammonium hydroxide may be illustrated by the following equation:—

$$\underset{\text{Ammonia}}{NH_3} + \underset{\text{Water}}{H_2O} = \underset{\text{Ammonium hydroxide}}{NH_4OH}$$

Solutions of Ammonia, prepared by the above process on a large scale and in suitable apparatus (bottles being so arranged in a series as to condense all the ammonia evolved during the operation), are used in pharmacy—the one (sp. gr. 0·891) containing 32·5 per cent., the other (sp. gr. 0·959) 10 per cent. by weight of ammonia, NH_3 (*Liquor Ammoniæ Fortis* and *Liquor Ammoniæ,* B.P. One part, *by measure,* of the former, and two of water are mixed in order to obtain the latter).

Spiritus Ammoniæ, U.S.P., is alcohol (91 per cent.) containing 10 per cent. by weight of ammonia, NH_3.

Ammonium Acetate

Experiment 3.—To acetic acid and water in a test-tube add commercial ammonium carbonate (acid carbonate and carbamate) until effervescence ceases, and the liquid, after well stirring or shaking, or perhaps warming, to get rid of carbonic anhydride, is only faintly acid to litmus (*see* p. 101). This solution, when of prescribed strength, forms the official Solution of Ammonium Acetate, $NH_4C_2H_3O_2$ (*Liquor Ammonii Acetatis,* B.P.). On evaporating and cooling, ammonium acetate may be obtained in crystals, but some of the salt will then have undergone decomposition into ammonia and acetic acid. In the rare case of *exact* neutrality being required, to the liquid which has been made slightly alkaline with excess of ammonium carbonate add acetic acid, finally drop by drop, until a drop of the resulting solution no longer gives a white precipitate with a drop of a clear solution of ordinary lead acetate (on a piece of glass backed by black paper or black cloth).

$$\underset{\text{Ammonium acid carbonate and carbamate}}{H_4HCO_3,NH_4NH_2CO_2} + \underset{\text{Acetic acid}}{3HC_2H_3O_2} = \underset{\text{Ammonium acetate}}{3NH_4C_2H_3O_2} + \underset{\text{Water}}{H_2O} + \underset{\text{Carbonic anhydride}}{2CO_2}$$

Solution of ammonium acetate can, of course, also be made by the interaction of acetic acid and solution of ammonia; but the liquid, owing to the absence of dissolved carbonic acid, is too vapid for medicinal use.

Ammonium Carbonates

Commercial ammonium carbonate is made by heating a mixture of calcium carbonate and ammonium chloride; calcium chloride, $CaCl_2$, remains, while water, H_2O, and some ammonia, NH_3, escape, and the ammoniacal carbonate distils or, rather, sublimes * in cakes (*Ammonii Carbonas*, B.P.). The best form of apparatus to employ is a retort with a short wide neck and a cool receiver. On the large scale the retort is usually iron, and the receiver earthenware or glass; on the small scale glass vessels are employed. The salt is purified by resublimation at a low temperature—150° F. (65·5° C) is said to be sufficient.

The salt, the empirical formula of which is $N_3H_{11}C_2O_5$, is probably a mixture of one molecule (sometimes two) of ammonium hydrogen carbonate (ammonium bicarbonate), NH_4HCO_3, and one of a salt termed ammonium carbamate, $NH_4NH_2CO_2$. The latter belongs to an important class of salts known as *carbamates*, but is the only one of direct interest to the pharmacist. Cold water extracts it from commercial ammonium carbonate, leaving the greater part of the bicarbonate undissolved if the amount of water used be very small. Alcohol also extracts the carbamate, leaving the bicarbonate undissolved. In contact with water the carbamate soon changes into normal ammonium carbonate:— $NH_4NH_2CO_2 + H_2O = (NH_4)_2CO_3$; so that an aqueous solution of commercial ammonium carbonate contains both hydrogen ammonium carbonate and normal ammonium carbonate. If to such a solution some ammonia be added, a solution of *normal ammonium carbonate* is obtained: this is the common reagent found on the shelves of the analytical laboratory. Thus, "Solution of Ammonium Carbonate," B.P., is prepared by dissolving the commercial salt in water to which solution of ammonia has been added.

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* *Sublimation* (from *sublimis*, high) is the term applied to the vaporization of a solid substance by heat, and its subsequent condensation on an upper and cooler part of the vessel or apparatus in which the operation is performed. The product of sublimation is called a *sublimate*. Different substances sublime at different temperatures, hence a mixture of volatile solids may sometimes be separated or fractionated by sublimation.

$$NH_4HCO_3,NH_4NH_2CO_2 + NH_4OH = 2(NH_4)_2CO_3$$

Normal ammonium carbonate is the salt formed on adding concentrated solution of ammonia to the commercial carbonate in preparing a pungent mixture for toilet smelling-bottles; but it is unstable, and on continued exposure to air is converted into a mass of crystals of bicarbonate.

If ammonium carbonate contain more than traces of empyreumatic matters (from the gas-liquor), an aqueous solution of it, with excess of sulphuric acid added, will at once decolorize a dilute solution of potassium permanganate.

Sal Volatile (*Spiritus Ammoniæ Aromaticus*, B.P.) is a spirituous solution of about 1¼ per cent. of ammonia, NH_3, nearly 3½ per cent. of normal ammonium carbonate, $(NH_4)_2CO_3$, with oils of nutmeg and lemon. Commercial samples contain salts equivalent to from 1 to nearly 3 per cent. of ammonia, the official spirit yielding a total of nearly 2½ per cent of the gas. Fetid spirit of ammonia (*Spiritus Ammoniæ Fetidus*, B.P.) is an lcoholic solution of the volatile oil of asafetida mixed with solution of ammonia.

Ammonium Nitrate

Experiment 4.—To some dilute nitric acid add "ammonium carbonate," until, after well stirring, a slightly ammoniacal odour remains. The solution contains ammonium nitrate.

$$NH_4HCO_3,NH_4NH_2CO_2 + 3HNO_3 = 3NH_4NO_3 + H_2O + 2CO_2$$

Ammonium hydrogen carbonate and carbamate — Nitric acid — Ammonium nitrate — Water — Carbonic anhydride

From a concentrated hot solution of ammonium nitrate, crystals may be obtained containing much water (NH_4NO_3, $2H_2O$). On heating these in a dish to about 320° F. (160° C.) the water escapes. The fused anhydrous salt remaining (NH_4NO_3) may be poured out on an iron plate. On further heating the fused nitrate, at 350° to 450° F. (about 177° to 32° C.), it is resolved into nitrous oxide or *laughing-gas* and water, $NH_4NO_3 = N_2O + 2H_2O$.

Nitrous oxide is prepared in this way for use as an anæshetic. When required for inhalation, it is washed from any race of nitric acid or nitric oxide by being passed through olution of potassium hydroxide and solution of ferrous sulphate, the former absorbing acid vapours, the latter nitric oxide. It is slightly soluble in warm water, more so in cold. It supports combustion almost as well as oxygen. By the application of sufficient pressure it may be reduced to a colourless liquid, and by simultaneous cooling it can be solidified. Inhalation of a *mixture* of nitrous oxide and air causes laughter or other excitement.

Ammonium Citrate, Phosphate, and Benzoate

Experiment 5.—To a solution of citric acid, $H_3C_6H_5O_7$, add solution of ammonia until the well-stirred liquid smells faintly of ammonia. This solution, when of prescribed strength and made with ammonium carbonate in order that it may contain a little carbonic acid and, hence, be less vapid for medicinal use, forms the official Solution of Ammonium Citrate, $(NH_4)_3C_6H_5O_7$ (*Liquor Ammonii Citratis*, B.P.). *Ammonium Phosphate*, $(NH_4)_2HPO_4$ (*Ammonii Phosphas*, B.P.), and *Ammonium Benzoate*, $NH_4C_7H_5O_2$ (*Ammonii Benzoas*, B.P.), are also made by adding solution of ammonia to phosphoric acid, H_3PO_4, and benzoic acid, $HC_7H_5O_2$, respectively, evaporating (keeping the ammonia in slight excess by adding more of its solution), and setting aside to crystallize.

$$\underset{\text{Citric acid}}{H_3C_6H_5O_7} + \underset{\substack{\text{Ammonium}\\ \text{hydroxide}}}{3NH_4OH} = \underset{\text{Ammonium citrate}}{(NH_4)_3C_6H_5O_7} + \underset{\text{Water}}{3H_2O}$$

$$\underset{\text{Phosphoric acid}}{H_3PO_4} + \underset{\substack{\text{Ammonium}\\ \text{hydroxide}}}{2NH_4OH} = \underset{\text{Ammonium phosphate}}{(NH_4)_2HPO_4} + \underset{\text{Water}}{2H_2O}$$

$$\underset{\text{Benzoic acid}}{HC_7H_5O_2} + \underset{\substack{\text{Ammonium}\\ \text{hydroxide}}}{NH_4OH} = \underset{\text{Ammonium benzoate}}{NH_4C_7H_5O_2} + \underset{\text{Water}}{H_2O}$$

Ammonium phosphate occurs in transparent colourless prisms, soluble in water, insoluble in alcohol; ammonium benzoate occurs in crystalline plates, soluble in water and in alcohol. An extended formula for ammonium benzoate is $C_6H_5{\cdot}COONH_4$; for ammonium citrate, $C_3H_4{\cdot}OH{\cdot}(COONH_4)_3$.

Ammonium Bromide, NH_4Br, (*Ammonii Bromidum*, B.P.), will be noticed in connection with Hydrobromic Acid and other Bromides. Ammonium Iodide, NH_4I, is included in the United States Pharmacopœia.

Ammonium Oxalate

Experiment 6.—To a nearly boiling solution of 1 part of oxalic acid in about 8 of water add ammonium carbonate until the liquid is neutral to *test-paper* (*see* following paragraphs), filter while hot, and set aside to crystallize. The product is Ammonium Oxalate, B.P., $(NH_4)_2C_2O_4$, H_2O, or $(COONH_4)_2$, H_2O. A solution of it is used as a reagent in analysis; 1 part of the pure salt in 40 of water forms "Solution of Ammonium Oxalate," B.P.

$$\underset{\text{Oxalic acid}}{3H_2C_2O_4} + \underset{\text{“Ammonium carbonate”}}{2N_3H_{11}C_2O_5} = \underset{\text{Ammonium oxalate}}{3(NH_4)_2C_2O_4} + \underset{\text{Carbonic anhydride}}{4CO_2} + \underset{\text{Water}}{2H_2O}$$

Neutralization.—Thus far the methods by which the student has avoided excess of either acid matter on the one hand, or alkaline on the other, have been the rough aid of taste, cessation of effervescence, presence or absence of odour, etc. More delicate aid is afforded by *test-papers.*

Test-papers.—*Litmus* (B.P.) is a blue vegetable pigment, prepared from various species of *Roccella* lichen, exceedingly sensitive to the action of acids, which turn it red. When thus reddened, alkalies (caustic potash or soda, and ammonia) and other soluble hydroxides, also alkali-metal carbonates, etc., readily turn it blue. The student should here test for himself the delicacy of this action by experiments with paper soaked in solution of litmus and dipped into very dilute solutions of acids, acid salts (*e.g.* $KHC_4H_4O_6$), alkalies, and such neutral salts as potassium nitrate, sodium sulphate, or ammonium chloride.

Solution of Litmus (B.P.).—This is prepared from purified litmus. Gently boil litmus with four times its bulk of alcohol (90 per cent.) for an hour. Pour away the fluid and repeat the operation twice. Digest the residual litmus in distilled water and filter.

Blue litmus-paper (B.P.) is "made by impregnating unglazed white paper with a solution of litmus." *Red litmus-paper* (B.P.) is "made by impregnating unglazed white paper with solution of litmus reddened by the previous addition of a very minute quantity of sulphuric acid."

Turmeric paper (B.P.) similarly prepared from Tincture of Turmeric (B.P.) (1 of turmeric root or rhizome to 6 of alcohol (90 per cent.), macerated for seven days), is occasionally useful as a test for alkalies, which turn its yellow to brown; acids do not affect it. Several other "indicators" of alkalinity or acidity are used, such as Solution of Methyl Orange, Solution of Phenol-phthalein, and Tincture of Cochineal.

Ammonium Hydrosulphide

Experiment 7.—Pass hydrogen sulphide, H_2S, through a small quantity of ammonia solution in a test-tube, until a portion of the liquid no longer causes a white precipitate in solution of magnesium sulphate; the product is a solution of ammonium hydrosulphide, NH_4SH, a valuable chemical reagent, as will presently be apparent:—

$$NH_4OH + H_2S = NH_4SH + H_2O$$

"Solution of Ammonium Hydrosulphide," B.P., is made by saturating 3 parts by measure of solution of ammonia with washed hydrogen sulphide, and then adding 2 parts by measure of solution of ammonia. The solution should be preserved in a well-stopped bottle.

Hydrogen Sulphide or *sulphuretted hydrogen* is a poisonous gas possessing an unpleasant odour; hence the above operation and many others, described farther on, in which this gas is indispensable, must be performed in the open air, or in a *fume-cupboard*—a chamber so contrived that noxious gases and vapours shall escape into a chimney in connection with the external air. In the above experiment, the small quantity of gas required can be made in a test-tube. Place some fragments of ferrous sulphide, FeS, in a test-tube, add water and then sulphuric acid; the gas is at once evolved, and may be conducted by a tube into the ammonia solution. Ferrous sulphate remains in solution in the generating tube:—

$$FeS + H_2SO_4 = H_2S + FeSO_4$$

As heat is not necessary in the preparation of sulphuretted hydrogen, "Hydrogen Sulphide," B.P., the test-tube of the foregoing operation may be advantageously replaced by a bottle, especially when larger quantities of the gas are required. In analytical operations, the gas should be purified by passing it through water contained in a second bottle.

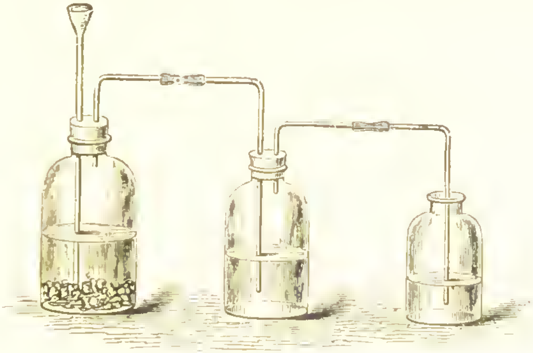


FIG. 20.—Hydrogen Sulphide Apparatus.

A convenient apparatus for experimental use is arranged as follows:—Two common wide-mouthed bottles are selected, the one having a capacity of about half a pint, the other a quarter pint; the former may be called the *generating-bottle*, the latter the *wash-bottle*. Fit both bottles with good sound corks. Through each cork bore two holes of such a size that glass tubing of about the diameter of a quill pen shall fit them tightly. Through one of the holes in the cork of the generating-bottle pass a funnel-tube, so that its extremity may nearly reach the bottom of the bottle. To the other hole adapt a piece of tubing, 6 inches long, and bent in the middle to a right angle. A similar "elbow-tube" is fitted to one of the holes in the cork of the wash-bottle, and another elbow-tube, one arm of which is long enough to reach to near the bottom of the wash-bottle, is fitted to the other hole. Removing the corks, two or three ounces of water are now poured into each bottle, an ounce or two of ferrous sulphide put into the generating-bottle, and the corks replaced. The elbow-tube of the generating-bottle is now attached by a short piece of indiarubber tubing to the long-armed elbow-tube of the wash-bottle, so that gas coming from the generator may pass through the water in the wash-bottle. The delivery-tube of the wash-bottle is then lengthened by attaching to it, by means of indiarubber tubing, another piece of glass tubing several inches in length. The apparatus is now ready for use. Concentrated sulphuric acid is poured down the funnel-tube in small quantities at a time, until brisk effervescence is established, and more is added from time to time as the evolution of gas becomes slow. The gas passes through the tubes into the wash-bottle, where, as it bubbles up through the water, any trace of sulphuric acid, or other matter mechanically carried over, is arrested, and thence the gas flows out at the delivery-tube into any vessel or liquid that may be placed there to receive it. The generator must be detached occasionally, and the ferrous sulphate washed out of it. Should difficulty be experienced in obtaining sufficiently sound corks to make gas-tight fittings for the apparatus, double-bored rubber stoppers, obtainable from any apparatus dealer, may be employed.

Hydrogen sulphide dissolves in water to a moderate extent, yielding a solution which smells strongly of the gas, and is frequently employed as a reagent. When the solution is exposed to air the hydrogen sulphide rapidly undergoes oxidation with deposition of white sulphur:—

$$2H_2S + O_2 = 2H_2O + S_2.$$

Analytical Reactions of Ammonium Salts.

1. To a solution of an ammonium salt (ammonium chloride, for example), in a test-tube, add solution of caustic soda (or caustic potash, or slaked lime), and warm the mixture; a characteristic odour (ammonia, NH_3) results: $NH_4Cl + NaOH = NH_3 + H_2O + NaCl$.

The recognition of the *odour* of ammonia is one of the readiest means of detecting the presence of this substance; but the following tests are occasionally useful. Into the upper part of the test-tube insert a glass rod moistened with concentrated hydrochloric acid (that is, with the aqueous solution of hydrochloric acid gas conventionally termed hydrochloric acid, the *Acidum Hydrochloricum* of the Pharmacopœia); white fumes of ammonium chloride will be produced:—$NH_3 + HCl = NH_4Cl$. Hold a piece of moist red litmus-paper in a tube from which ammonia is being evolved; the red colour will be changed to blue.

Though ammonium itself cannot be obtained in the free state, its compounds are stable. As the foregoing experiment shows, ammonia is easily expelled from these compounds by the action of the stronger alkalies, caustic potash, caustic soda, or slaked lime. As a useful exercise, the student should here construct equations in which ammonium acetate, $NH_4C_2H_3O_2$, sulphate, $(NH_4)_2SO_4$, nitrate, NH_4NO_3, or any other ammonium salt, is supposed to be under examination; also equations representing the use of the other hydroxides, KOH or $Ca(OH)_2$.

2. To a few drops of a solution of an ammonium salt, add a drop or two of chloroplatinic acid, H_2PtCl_6: a yellow crystalline precipitate of ammonium chloroplatinate, $(NH_4)_2PtCl_6$, will be produced, similar in appearance to the corresponding potassium salt, the remarks concerning which (*see* p. 81) are equally applicable to the precipitate under notice.

3. To a moderately concentrated solution of an ammonium salt add a saturated solution of sodium hydrogen tartrate, and shake or well stir the mixture; a white granular precipitate of ammonium hydrogen tartrate (acid ammonium tartrate) will be formed.

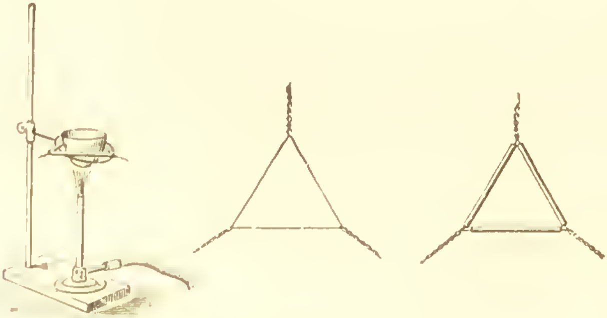
For data from which to construct an equation representing this action, see the remarks and formulæ under the analogous potassium salt (p. 82).

4. Evaporate a few drops of a solution of an ammonium salt to dryness, or place a fragment of a solid ammonium salt on a piece of platinum foil, and heat in a flame; the salt is readily *volatilized*, usually with decomposition (*see* p. 106). As already noticed, the salts of potassium and sodium are *fixed* (*i.e.*, non-volatile) under these circumstances, a point of difference of

which advantage is frequently taken in analysis. A porcelain crucible may often be advantageously substituted for platinum foil in experiments on volatilization.

Salts of ammonium with the more complex acid radicals seldom volatilize unchanged when heated. The oxalate, when so treated, loses its water of crystallization, and at a higher temperature decomposes, yielding carbonic oxide, carbonic anhydride, ammonia gas, water, and several organic substances. The phosphate loses water and ammonia, and yields a residue of metaphosphoric acid.

A wire triangle may be used in supporting crucibles (fig. 21). It is made by twisting together each pair of ends of three (5- or 6-inch) crossed pieces of wire (fig. 22). A piece of tobacco-pipe stem (about 2 inches) is sometimes placed in the middle of each wire before twisting, the transference of any metallic matter to the sides of the crucible being thereby prevented (fig. 23).



FIGS. 21, 22, 23.—Triangular Supports for Crucibles.

LITHIUM: Li. Atomic weight, 6·97

Lithium is widely distributed in nature, but is usually in minute proportions as compared with other elements. A trace of it may be found in most soils and waters, a certain spring in Cornwall containing even considerable quantities as chloride.

Lithium carbonate, Li_2CO_3 (*Lithii Carbonas*, B.P.), is a white granular powder obtained from the minerals which contain lithium—namely, lepidolite (from λεπίς, *lepis*, a scale, and λίθος, *lithos*, a stone, referring to its scaly appearance);

triphane (from τρεῖς, *treis*, three, and φαίνω, *phainō*, I shine) or spodumene (from σποδόω, *spodŏō*, I reduce to ashes, in allusion to its exfoliation in the blowpipe-flame); and petalite (from πέταλον, *petalon*, a leaf, referring to its laminated character). Each contains aluminium silicate, with potassium and lithium fluoride in the case of Austrian lepidolite (which is the most abundant source) and sodium and lithium silicates in the others. To separate the lithium, lepidolite is decomposed by sulphuric acid; alumina, etc., precipitated by ammonia; the filtrate evaporated and the residue ignited. The resulting sulphates are dissolved in water and lithium carbonate is precipitated by adding a solution of a carbonate. The preparation of common alum is sometimes made a part of the factory processes. *Lithii Carbonas*, B.P., should yield "only the slightest reactions with the tests for calcium and for sulphates." It is soluble in 68 parts of water at 15° C. and in 131 at 100° C.

Lithium citrate (*Lithii Citras*, B.P.) is used in medicine. It occurs in white deliquescent crystals or powder, "prepared by saturating citric acid with lithium carbonate." The crystals have the formula $Li_3C_6H_5O_7, 4H_2O$; dried at 212° F. (100° C.), $Li_3C_6H_5O_7, H_2O$ (Umney).

$$\underset{\substack{\text{Lithium}\\ \text{carbonate}}}{3Li_2CO_3} + \underset{\text{Citric acid}}{2H_3C_6H_5O_7} = \underset{\substack{\text{Lithium}\\ \text{citrate}}}{2Li_3C_6H_5O_7} + \underset{\text{Water}}{3H_2O} + \underset{\substack{\text{Carbonic}\\ \text{anhydride}}}{3CO_2}$$

Lithium citrate should yield by incineration 52·8 per cent. of white lithium carbonate. *Lithii Citras Effervescens*, B.P., is prepared by mixing lithium citrate with citric and tartaric acids and sodium bicarbonate, then heating and stirring until the mixture assumes a granular character.

Additional salts of lithium, included in the United States Pharmacopœia, are *Lithii Benzoas*, U.S.P., $LiC_7H_5O_2$; *Lithii Bromidum*, U.S.P., LiBr; and *Lithii Salicylas*, U.S.P., $LiC_7H_5O_3$.

Lithium urate[*] is more soluble than sodium urate; hence lithium preparations are administered to gouty patients in the hope (apparently quite unintelligible on any chemical grounds) that sodium urate, with which such systems are loaded, may be converted into lithium urate and removed.

In its analytical behaviour, lithium stands in some respects between the alkali-metals potassium and sodium, and the metals of the barium group (barium, strontium, and calcium), its hydroxide, carbonate, and phosphate being only slightly soluble in water. Lithium chloroplatinate, Li_2PtCl_6, is soluble in water and in alcohol. The atom of lithium is univalent, $Li^{\cdot}$.

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[*] Urates will be considered subsequently in connection with uric acid.

Analytical Reactions of Lithium Salts.

1. To a solution of lithium chloride, LiCl (obtained by dissolving a few grains of lithium carbonate in dilute hydrochloric acid), add a solution of ordinary sodium phosphate, Na_2HPO_4, and a little sodium hydroxide, or ammonia, and boil. A white crystalline precipitate of lithium phosphate is produced :—

$$3LiCl + Na_2HPO_4 + NaOH = Li_3PO_4 + 3NaCl + H_2O$$

2. Moisten the end of a platinum wire with a solution of a lithium salt, and introduce it into the flame of a Bunsen burner or spirit-lamp; a magnificent crimson tinge is imparted to the flame.

The light thus emitted by incandescent lithium vapour is of a purer crimson than that given by strontium. When the flames are examined by means of the spectroscope the red rays are, in the case of strontium, found to be associated with blue and yellow, neither of which is observed in the lithium light.

Qualitative Analysis.

With regard to those of the preceding experiments which are useful rather as means of detecting the presence of potassium, sodium, ammonium, and lithium (the so-called "tests"), than as illustrating the preparation of salts, the student should proceed to apply them to certain solutions of any of the salts of these metallic radicals with the view of ascertaining which radical is present; that is, proceed to *practical analysis.** A little thought will enable him to apply

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* Such solutions are prepared in educational laboratories by a tutor. They should, under other circumstances, be mixed by a friend, as it is not desirable for the student to know previously what is contained in the substance he is about to analyse.

The analysis of solutions containing only one salt serves to impress the memory with the characteristic tests for the various metallic and other radicals, and familiarize the mind with chemical the reactions in the most suitable order and to the best advantage for the contemplated purpose; but the following arrangements are perhaps as good as can be devised:—

DIRECTIONS FOR APPLYING THE ANALYTICAL REACTIONS DESCRIBED IN THE FOREGOING PARAGRAPHS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF A SALT OF ONE OF THE METALLIC RADICALS, POTASSIUM, SODIUM, AMMONIUM, LITHIUM.

To a small portion of the solution to be examined, in a test-tube, add caustic soda, and warm the mixture; the odour of ammonia gas reveals the presence of an ammonium salt.

To a few drops of the solution, apply the bismuth thiosulphate test for potassium (p. 82); a yellow precipitate indicates the presence of potassium. Potassium may also be detected by means of the chloroplatinic acid test, but only in the known absence of ammonium salts.

The flame-test is sufficient for the recognition of sodium or of lithium.

DIRECTIONS FOR APPLYING THE ANALYTICAL REACTIONS DESCRIBED IN THE FOREGOING PARAGRAPHS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ONE OR MORE OF THE ALKALI-METALS.

I. In cases when it is not necessary to effect actual separation of the metallic radicals present, the examination of the solution may best be carried out by making special tests for each of them as below:

To a small portion of the solution in a test-tube, add caustic soda and warm the mixture; the odour of ammonia reveals the presence of an ammonium salt.

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principles. Medical students seldom have time to go farther than this. More thorough analytical and general chemical knowledge is only acquired by working on such mixtures of substances as are met with in actual practice, beginning with solutions which may contain any or all of the members of a group. Hence in this Manual two tables of short analytical directions are given under each group. Pharmaceutical students should follow the second.

Apply the bismuth thiosulphate test for potassium to a few drops of the solution (p. 82). The formation of a yellow precipitate indicates the presence of a potassium salt.*

To another portion of the solution add sodium phosphate and then ammonia until the liquid, after shaking, smells of ammonia, and boil. The formation of a white precipitate indicates the presence of a lithium salt. Test for lithium also by the flame-test.

The flame-test is sufficient for the recognition of sodium unless it is present in small quantity along with much lithium. In such a case the spectroscope may be employed. Traces of lithium may also be detected in presence of much sodium by means of the spectroscope.

Note on the flame-test.—When the violet tint imparted to the flame by potassium salts is masked by the intense yellow colour due to sodium, it may still be recognised, in the absence of lithium salts, if the flame be observed through a piece of dark-blue glass, a medium which absorbs the yellow rays of light but allows the violet rays to pass. It is not safe to examine a solution for potassium by the flame-test in the known presence of lithium salts.

II. Should it be necessary actually to separate the metallic radicals from one another, the analysis may be carried out according to the following method:—

Commence by testing a small portion of the solution for an ammonium salt; if it be present it must be got rid of prior to testing for (and if present, removing) potassium as chloroplatinate. Evaporate the remainder of the original solution to dryness in a small basin, transfer the solid residue, by instalments if necessary, to a porcelain crucible, and heat the latter to low redness until white fumes, due to the decomposition of ammonium salts, no longer escape (*see* fig. 19). This operation should be conducted in a fume-cupboard, to avoid contamination of the air of the laboratory. When the crucible has cooled, dissolve the solid residue in a small quantity of hot water, filter if necessary, add excess of chloroplatinic acid (*i.e.*, add sufficient of the reagent to convert the whole of the alkali-metals present into chloroplatinates) and evaporate to dryness on a water-bath, or at any rate at a temperature not exceeding 100° C. Digest the residue for some time with alcohol, and filter :—

---

* If an ammonium salt be present, it is desirable to get rid of it as described under II., before applying this test for potassium.

<table>
<tr><td colspan="2"><i>Residue.</i>—A heavy yellow powder consisting of potassium chloroplatinate, K_2PtCl_6. Wash with alcohol ; dry ; transfer to a porcelain crucible, and heat gradually up to redness. Treat the residue with hot water, and filter :</td><td colspan="3"><i>Filtrate.</i>—May contain sodium and lithium chloroplatinates, with excess of chloroplatinic acid. Evaporate or distil off the alcohol, and heat to redness the brown solid which remains. Treat the residue with hot water, and filter :</td></tr>
<tr><td rowspan="2"><i>Residue.</i>—Consists of platinum.</td><td rowspan="2"><i>Filtrate.</i>—Contains potassium chloride. Confirm potassium by the flame-test.</td><td rowspan="2"><i>Residue.</i> Consists of platinum.</td><td colspan="2"><i>Filtrate.</i>—May contain NaCl and LiCl. Evaporate to dryness. Treat repeatedly with alcohol, filtering each instalment.</td></tr>
<tr><td><i>Residue.</i>—NaCl ; confirm by flame-test.</td><td><i>Filtrate.</i>—May contain LiCl. Apply flame-test.</td></tr>
</table>

Note on Nomenclature.—The operations of *evaporation* and heating to redness, commonly termed *ignition*, are frequently necessary in analysis, and are usually conducted in the above manner. If vegetable or animal matter be present also, carbon is set free, and ignition is accompanied by *carbonization* ; the material is said to *char*. When all carbonaceous matter is burnt off (the crucible being slightly inclined and its cover removed to facilitate combustion), and mineral matter, or *ash*, alone remains, the operation of *incineration* has been effected.

Note on the Classification of the Elements.—The compounds of potassium, sodium, ammonium, and lithium, have many analogies. The carbonates, phosphates, and other common salts are soluble in water, except lithium carbonate and phosphate, which are only sparingly soluble. Atoms of the metallic radicals are univalent—that is, each displaces or is displaced by one atom of hydrogen. In fact, these radicals constitute by their similarity in properties a distinct group or family. All the elements thus naturally fall into classes—

a fact that should constantly be borne in mind, and evidence of which should always be sought. It would be impossible for the memory to retain the details of Chemistry without a system of classification and leading principles. Classification is also an important feature in the art as well as in the science of Chemistry; for without it practical analysis could not be undertaken. The classification adopted in this volume is founded on the quantivalence of the elements (or radicals) and on their analytical and general relations.

QUESTIONS AND EXERCISES

Why are ammonium salts classed with those of potassium and sodium? Mention the sources of the ammonium salts.—Describe the characters of Ammonium Chloride.—Give the formula of Ammonium Sulphate.—Adduce evidence of the existence of Ammonium.—How is Solution of Ammonia prepared?—How is the official Solution of Ammonium Acetate prepared?—What is the composition of commercial Ammonium Carbonate?—Define *sublimation.*—What ammonium salts are contained in *Spiritus Ammoniæ Aromaticus*, B.P., and *Spiritus Ammoniæ Fœtidus*, B.P.?—Give diagrams or equations illustrating the formation of Ammonium Citrate (from hydroxide and from carbonate), Phosphate, and Benzoate.—Give the formula of Ammonium Oxalate.—How is ammonium hydroxide converted into hydrosulphide?—Describe the preparation of Hydrogen Sulphide.—Enumerate and explain the tests for ammonium. How is potassium detected in a solution in which ammonium has been found?—Give equations illustrating the action of sodium hydroxide on ammonium acetate; potassium hydroxide on ammonium sulphate; and calcium hydroxide on ammonium nitrate.—Name the sources and official compounds of lithium.—Explain the formation of lithium citrate.—On what chemical hypothesis are lithium compounds administered to gouty patients?—What are the chief tests for lithium?—Describe the analysis of an aqueous liquid containing salts of potassium, sodium, ammonium, and lithium.—What meanings are commonly assigned to the terms *evaporation*, *ignition*, *carbonization*, and *incineration?*—Write a short article descriptive of the analogies of potassium, sodium, ammonium, and lithium, and their compounds.

BARIUM, STRONTIUM, CALCIUM, MAGNESIUM

These four elements have many analogies. Their atoms are bivalent—$\mathrm{Ba}^{\prime\prime}$, $\mathrm{Sr}^{\prime\prime}$, $\mathrm{Ca}^{\prime\prime}$, $\mathrm{Mg}^{\prime\prime}$.

BARIUM : Ba. Atomic weight, 136·4

It is the analytical reactions of this metal which are of chief interest to the student of pharmacy. Barium nitrate, $Ba(NO_3)_2$, and chloride, $BaCl_2, 2H_2O$ (Barium Chloride, B.P., and "Solution of Barium Chloride," B.P., 1 in 10 of water) are the soluble salts in common use in analysis. These and other salts are made by dissolving the native carbonate, $BaCO_3$ (the mineral *witherite*) in acids, or by heating the other common natural compound of barium, the sulphate (*heavy white* or *heavy spar*, $BaSO_4$) with coal, which yields barium sulphide, BaS ($BaSO_4 + 4C = 4CO + BaS$), and treating this with appropriate acids. When the nitrate is strongly heated, it decomposes, yielding barium oxide or *baryta*, BaO. By intensely heating a mixture of barium sulphate and carbon in the electric furnace, barium oxide mixed with a small proportion of sulphide is now prepared on a large scale. Baryta, on being moistened, unites with the elements of water with the evolution of much heat, and yields barium hydroxide, $Ba(OH)_2$. The latter is tolerably soluble, giving *baryta water;* and from this solution crystals of barium hydroxide, $Ba(OH)_2,8H_2O$, are obtained on evaporation. Barium hydroxide is largely used in the refining of sugar.

Barium peroxide, BaO_2, is formed on passing air over barium oxide heated to about 600° C. At a somewhat higher temperature, oxygen is evolved and barium oxide remains. This is Boussingault's old process; but, after a time, the barium oxide loses its power of combining with additional oxygen. If the air be freed from carbonic anhydride, and the peroxide be not exposed to a much higher temperature than 800° C., the barium oxide can be used over and over again. The air is passed over it under increased pressure, and gives rise to the formation of the peroxide. The air is then turned off, and the additional oxygen is given up again when the pressure is sufficiently reduced by means of air-pumps. This improvement is used in the process of Messrs Brin, who sell the oxygen compressed within strong steel cylinders.

Hydrogen Peroxide.—By the action of a dilute acid, barium peroxide yields a solution of *hydrogen peroxide*, H_2O_2, formerly called *oxygenated water*. An aqueous solution of hydrogen peroxide which yields (by the decomposition of the peroxide) ten times its volume of oxygen, is the official

Liquor Hydrogenii Peroxidi, B.P., "1 volume, treated in a brine-charged nitrometer with ten or twelve times its bulk of a mixture of 1 volume of sulphuric acid, 2 volumes of a five per cent. solution of potassium permanganate, and 7 volumes of water, should afford, at normal temperature and pressure, not less than 18, and not more than 22 volumes of oxygen, indicating a yield of 9 to 11 volumes from the solution of hydrogen peroxide":

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = 5O_2 + 8H_2O + K_2SO_4 + 2MnSO_4$$

One half of the oxygen comes from the peroxide, and one half from the permanganate. The peroxide readily yields oxygen to many inorganic and organic substances.

Barii Dioxidum and *Aqua Hydrogenii Dioxidi* are included in the United States Pharmacopœia.

Analytical Reactions of Barium Salts.

1. To the aqueous solution of any soluble barium salt (nitrate or chloride, for example) add dilute sulphuric acid; a white precipitate is obtained. Set the test-tube aside for two or three minutes, and when some of the precipitate has fallen to the bottom, pour away the supernatant liquid, wash the precipitate by adding water, shaking, setting aside, and again decanting; and then add moderately concentrated nitric acid, and boil; the precipitate is insoluble. The precipitate is at once produced by the addition of a solution of calcium sulphate or other soluble sulphate.

The production of a white precipitate by sulphuric acid or other sulphate, insoluble even in hot nitric acid, is highly characteristic of barium. The precipitate consists of barium sulphate, $BaSO_4$.

2. To a solution of a barium salt add solution of potassium chromate, K_2CrO_4; a pale-yellow precipitate of barium chromate, $BaCrO_4$, is immediately formed. Add acetic acid to a portion; it is insoluble. Add hydrochloric or nitric acid to another portion; it dissolves.

Potassium bichromate or anhydrochromate, K_2CrO_4, CrO_3, or $K_2Cr_2O_7$, must not be used in this reaction, otherwise the barium will be only partially precipitated, as the bichromate gives rise to the formation of free acid, in which barium chromate is to some extent soluble:—

$$K_2CrO_4, CrO_3 + 2BaCl_2 + H_2O = 2BaCrO_4 + 2KCl + 2HCl$$

Other Analytical Reactions.—To a solution of a barium salt add a solution of a carbonate (ammonium carbonate, $(NH_4)_2CO_3$, will generally be rather more useful than the others); a white precipitate of barium carbonate, $BaCO_3$, is formed. To another portion of the solution add an alkali-metal phosphate (sodium phosphate, Na_2HPO_4, is the most common of these chemically analogous salts, but ammonium phosphate $(NH_4)_2HPO_4$, is often used in preference); white barium hydrogen phosphate, $BaHPO_4$, is precipitated, insoluble in pure water, but slightly soluble in aqueous solutions of some salts, and readily soluble even in acetic and other weak acids. To another portion add ammonium oxalate, $(NH_4)_2C_2O_4$; white barium oxalate, BaC_2O_4, is precipitated, soluble in dilute mineral acids, and sparingly so in acetic acid. Barium salts, moistened with hydrochloric acid, impart a greenish colour to a Bunsen flame or spirit-lamp flame.

Memorandum.—Good practice will be found in writing out equations to represent each of the foregoing reactions.

Antidotes.—In cases of poisoning by soluble barium salts, obvious antidotes would be solution of alum or of such sulphates as those of magnesium (Epsom salt) and sodium (Glauber's salt).

QUESTIONS AND EXERCISES

What is the valency of barium?—Write the formulæ of barium oxide, hydroxide, chloride, nitrate, and sulphate; and state how the substances are prepared. Describe the preparation of hydrogen peroxide.—Which of the tests for barium are most characteristic?—Give equations for the reactions.—Name the antidote in cases of poisoning by soluble barium salts, and explain its action.

STRONTIUM: Sr. Atomic weight, 86·94

Occurrence.—Strontium compounds are not abundant in nature; yet the carbonate, $SrCO_3$, known as *strontianite,* and the sulphate, $SrSO_4$, known as *celestine* (from *cælum,* the sky, in allusion to its occasional bluish colour), are by no means rare minerals.

Salts of strontium are occasionally employed in medicine, the following being official in the United States Pharmacopœia:—*Strontii Bromidum,* $SrBr_2,6H_2O$; *Strontii Iodidum,* $SrI_2,6H_2O$; *Strontii Lactas,* $Sr(C_3H_5O_3)_2,3H_2O$. The compounds of this metal are, however, chiefly used by firework-manufacturers in preparing "red fire." Strontium hydroxide, like barium hydroxide, is much used in sugar-refining. Strontium salts impart a crimson colour to the flame. Strontium nitrate, $Sr(NO_3)_2$, is the most suitable strontium salt to use in making pyrotechnic mixtures, its oxygen causing vigorous combustion when the salt is mixed with charcoal, sulphur, etc., and heated. This salt may be obtained by dissolving the carbonate in nitric acid; a method which is appropriate for the preparation of other strontium salts if the corresponding acids are employed. Strontium salts may also be prepared from the cheaper strontium sulphate, $SrSO_4$, by strongly heating this with carbon to convert it into sulphide, SrS, and then dissolving the latter in the appropriate acids. Strontium sulphate is very sparingly soluble in water.

Analytical Reactions of Strontium Salts.

1. To a solution of strontium nitrate or chloride add ammonium carbonate; a white precipitate of strontium carbonate, $SrCO_3$, is produced.

2. To a solution of a strontium salt add highly dilute sulphuric acid, or an equally dilute solution of any sulphate (that of calcium, for example); a white precipitate of strontium sulphate, $SrSO_4$, is produced. The formation of this precipitate is promoted by stirring and by setting the liquid aside for some time. (Barium salts give an immediate precipitate under similar circumstances.)

3. To a dilute solution of a strontium salt add potassium chromate; no precipitate is produced unless the mixture is allowed to stand for some time, or is boiled.

Barium may be separated from strontium by means of potassium chromate, this reagent at once precipitating barium from aqueous or acetic acid solutions. The value of the reaction is enhanced if acetic acid or ammonium acetate be present, strontium chromate being far more soluble in such fluids than in water (Ransom). It is also more soluble in cold than in hot solutions.

4. Moisten the end of a platinum wire with a solution of a strontium salt and hold it in the Bunsen flame; a crimson colour is imparted to the flame.

Other Analytical Reactions.—Alkali-metal phosphates and oxalates give white insoluble precipitates with strontium salts as with barium (and also with calcium) salts.

CALCIUM: Ca. Atomic weight, 39·71

Occurrence, etc.—Calcium compounds form a large proportion of the crust of our earth. Calcium carbonate is met with as chalk, marble, limestone, calc-spar, etc.; the sulphate as gypsum and alabaster; the silicate in many minerals; calcium fluoride as fluor-spar. The phosphate is also a common mineral. Plaster of Paris (*Calcii Sulphas Exsiccatus*, U.S.P.) is gypsum from which the water of crystallization has been driven away by heating to a temperature of dull redness. The element itself is only isolated with great difficulty. Its melting point is 760° C.; its sp. gr. 1·85.

Calcium Chloride

Experiment 1.—To some hydrochloric acid add calcium carbonate (chalk, or the purer form, white marble), $CaCO_3$, until effervescence ceases; filter; solution of calcium chloride, $CaCl_2$, a common soluble calcium salt, is formed.

$$\underset{\substack{\text{Calcium}\\\text{carbonate}}}{CaCO_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid}}}{2HCl} = \underset{\substack{\text{Calcium}\\\text{chloride}}}{CaCl_2} + \underset{\text{Water}}{H_2O} + \underset{\substack{\text{Carbonic}\\\text{anhydride}}}{CO_2}$$

This solution may be obtained quite neutral by well boiling before filtering off the excess of marble.

Solution of calcium chloride evaporated to a syrupy consistence yields crystals ($CaCl_2,6H_2O$). These are extremely deliquescent. The solution, evaporated to dryness, and the white residue heated to about 392° F. (200° C.), gives solid calcium chloride, $CaCl_2,2H_2O$ (*Calcii Chloridum*, B.P.), in a porous form. The resulting lumps are used for drying gases and for freeing certain liquids from water. Calcium chloride is soluble in alcohol.

Marble often contains ferrous carbonate, $FeCO_3$, which in the above process becomes converted into ferrous chloride, rendering the calcium chloride impure:—

$$\underset{\substack{\text{Ferrous}\\\text{carbonate}}}{FeCO_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid}}}{2HCl} = \underset{\substack{\text{Ferrous}\\\text{chloride}}}{FeCl_2} + \underset{\text{Water}}{H_2O} + \underset{\substack{\text{Carbonic}\\\text{anhydride}}}{CO_2}$$

If pure calcium chloride be required, a few drops of the solution should be poured into a test-tube or beaker, diluted with water, and examined for iron (by adding ammonium hydrosulphide, which gives a black precipitate with iron salts), and, if the latter is present, calcium hypochlorite (in the form of chlorinated lime) and slaked lime should be added to the remainder of the liquid, and the whole boiled for a few minutes. The iron is precipitated as ferric hydroxide, and is filtered off:—

$$\underset{\substack{\text{Ferrous}\\\text{chloride}}}{4FeCl_2} + \underset{\substack{\text{Calcium}\\\text{hypochlorite}}}{Ca(ClO)_2} + \underset{\substack{\text{Calcium}\\\text{hydroxide}}}{4Ca(OH)_2} + \underset{\text{Water}}{2H_2O} = \underset{\substack{\text{Ferric}\\\text{hydroxide}}}{4Fe(OH)_3} + \underset{\substack{\text{Calcium}\\\text{chloride}}}{5CaCl_2}$$

The solution of calcium chloride so obtained may contain some calcium chlorate. On adding excess of ammonium carbonate and heating gently, then washing the precipitate thoroughly with hot water (*see* p. 120) and redissolving it in hydrochloric acid, a pure solution of calcium chloride may be obtained.

This process may be imitated on the small scale after adding a minute piece of iron to a fragment of the marble before dissolving in acid.

Calcium Oxide. Quicklime. Caustic Lime

Experiment 2.—Place a small piece of chalk in a strong fire or furnace, and heat until a fragment, chipped off and cooled, does not effervesce on the addition of acid; lime, CaO (*Calx*, B.P.), remains:—

$$\underset{\text{Calcium carbonate (chalk)}}{CaCO_3} = \underset{\text{Calcium oxide (lime)}}{CaO} + \underset{\text{Carbonic anhydride}}{CO_2}$$

Lime-kilns.—On a large scale the above operation is carried on in what are termed *lime-kilns* (*Kiln*, Saxon *cyln*, from *cylene*, a furnace).

Calcium Hydroxide. Slaked Lime

Experiment 3.—When the quicklime prepared in the preceding experiment is cold, add to it about half its weight of water, and notice the evolution of steam, and the other evidence of energetic chemical action; the product is slaked lime, calcium hydroxide, $Ca(OH)_2$ (*Calcii Hydras*, B.P.), with whatever slight natural impurities the lime may contain. The slaking of hard or "stony" lime may be accelerated by using hot water.

$$\underset{\text{Lime}}{CaO} + \underset{\text{Water}}{H_2O} = \underset{\text{Calcium hydroxide}}{Ca(OH)_2}$$

Lime-water.—Place the calcium hydroxide (washed with a little water to remove traces of soluble salts) in about a hundred times its weight of water, and shake frequently; in a short time a saturated solution, known as *lime-water* (*Liquor Calcis*, B.P.), results. It contains about 13 grains of calcium hydroxide, $Ca(OH)_2$, equivalent to about 10 grains of lime, (CaO), in one pint at 60° F. (15·5 C.). At higher temperatures less is dissolved.

Saccharated Solution of Lime.—Slaked lime is much more soluble in aqueous solution of sugar than in pure water. The *Liquor Calcis Saccharatus*, B.P., is such a solution, containing 2 ounces of sugar, and 188 grains of calcium hydroxide, $Ca(OH)_2$, equivalent to 142 grains of lime ((CaO), in 1 pint. It is a more efficient precipitant of hydroxides, carbonates, and phosphates than lime-water. The official process is as follows:—Mix the calcium hydroxide with a solution of the refined sugar in the distilled water. Set aside in a stoppered green glass bottle for a few hours, shaking occasionally. Separate the clear solution with a siphon, avoiding unnecessary exposure to air.

Solutions of calcium hydroxide absorb carbonic anhydride on exposure to air, a semi-crystalline precipitate of calcium carbonate being deposited. When the saccharated solution is heated, there is precipitated a compound consisting of three molecules of lime with one of sugar. When it is freely exposed to air, oxygen is absorbed, and the solution becomes coloured.

Calcium Carbonate

Experiment 4.—To a solution of calcium chloride add excess of sodium carbonate, or about 13 parts of the carbonate to 5 of the anhydrous chloride; a white precipitate of calcium carbonate, $CaCO_3$ (*Calcii Carbonas Præcipitatus*, B.P.), is produced. If the solutions of the salts be heated before admixture, and the whole be set aside for a short time, the particles assume a finely granular or slightly crystalline character to a greater extent than when cold water is used.

$$\underset{\substack{\text{Calcium}\\\text{chloride}}}{CaCl_2} + \underset{\substack{\text{Sodium}\\\text{carbonate}}}{Na_2CO_3} = \underset{\substack{\text{Calcium}\\\text{carbonate}}}{CaCO_3} + \underset{\substack{\text{Sodium}\\\text{chloride}}}{2NaCl}$$

Collect and purify this so-called *Precipitated Chalk* by pouring the mixture into a filter-paper supported by a funnel, and when the liquid has passed through the filter, pour water over the precipitate three or four times, until the whole of the sodium chloride is washed away. This operation is termed *washing a precipitate.* When dried by aid of a *water-bath* (p. 124) or other means, the precipitate is fit for use. It is not only somewhat purer than the average samples of natural chalk or "prepared chalk" (*see* p. 122), but it is less liable to aggregate, and on account of its physical characteristics is far superior as a constituent of dentifrices.

Filter-paper or *bibulous paper* (from *bibo*, I drink), is simply good unsized paper made from the best white rags—white blotting-paper, in fact, of unusually good quality. Students' or analysts' filters, on which to collect precipitates, are *circular* pieces (*a*, fig. 24), of this paper, from three to six inches in diameter, twice folded (*b*, *c*), and then opened out so as to form a hollow cone (*d*). The cone is supported by a glass or earthenware funnel. Square pieces of filter-paper should be rounded by scissors *after* twice folding. If this is not done, angular portions of the paper project above the liquid in the filter, and if a spirituous or other volatile liquid is being passed through such a paper, much of the liquid will be wasted by evaporation from the unnecessarily large surface exposed.

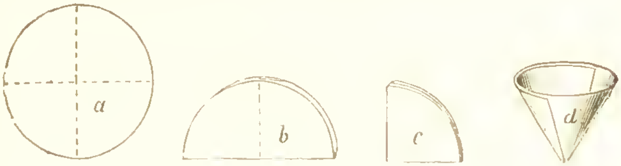


FIG. 24.—Construction of Paper Filters.

Paper filters of large size are apt to break at the point of the cone. This may be prevented, and the rate of filtration much accelerated, by supporting the paper cone in a cone of muslin.

Wash-bottle.—Precipitates are best washed by means of a fine jet of water directed on to the different parts of the filter. A common, narrow-necked bottle, of about half-pint capacity, is fitted with a cork; two holes are bored through the cork, the one for a glass tube which reaches to the bottom of the bottle and is bent externally to a slightly acute angle, the other for a tube bent to a slightly obtuse angle, the inner arm terminating just inside the bottle. The outer arms may be about three inches in length. The extremity of the outer arm of the longer tube should be previously drawn out to a fine capillary opening by holding the original tube (before bending it) in a flame, and, when soft, slowly pulling the two ends apart from each other until the softened portion is reduced to the diameter of a knitting-needle. The tube is now cut at the narrow part by means of a file, and the sharp edge rounded off by

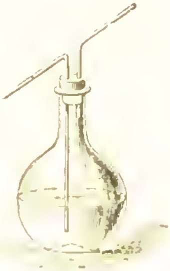
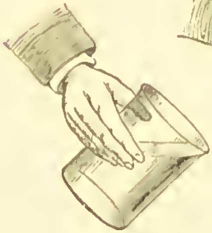
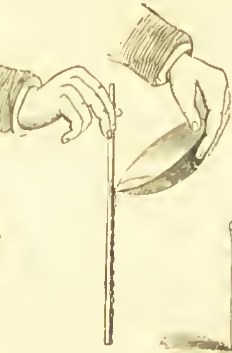


FIG. 25. Hot-water Wash-bottle.

placing it in a flame for a second or two. The outer extremity of the shorter tube should also be rounded off in the flame. The apparatus being put together, and the bottle nearly filled with water, air from the lungs, blown through the short tube, forces water out in a fine stream at the capillary orifice.

For a hot-water wash-bottle (fig. 25) the tubes and cork are fitted to a flask which may be heated over a Bunsen burner or on a water-bath (p. 124). Fine twine wound closely round the neck of the flask forms a suitable non-conducting protection for the hand of the operator.





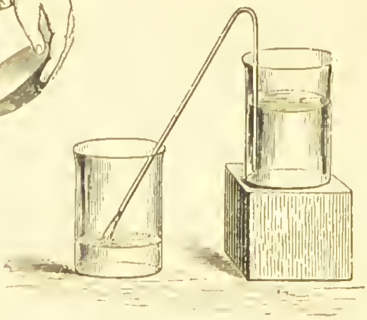


FIG. 26. Decantation. FIG. 27.—Decantation. FIG. 28.—Siphon in action.

Decantation.—Precipitates may also be washed by allowing them to settle, pouring off the supernatant liquid (fig. 26) agitating with water, again allowing to settle, and so on. This is washing by *decantation* (*de*, from ; *canthus*, an edge). If the stream of liquid exhibits any tendency to run down the outer side of the vessel during decantation, it should be guided by a glass rod placed against the point where the stream emerges (fig. 27).

If the vessel be too large to handle with convenience, the liquid may be drawn off by means of a *siphon*, as shown in fig. 28.

Prepared chalk (*Creta Præparata*, B.P.) is merely washed chalk or *whiting*, but in pharmacy, fashion demands that the chalk be in little conical lumps, about the size of thimbles, instead of in the larger rolls characteristic of whiting. Its powder is amorphous.

If either the precipitated or the prepared chalk contains alumina, magnesium salts, iron oxide, or phosphates, its solution in acid, evaporated to dryness, and redissolved in water, will yield a precipitate of hydroxides or phosphates on the addition of saccharated solution of lime.

Calcium Phosphate

Experiment 5.—Digest bone-ash (bones burnt in an open crucible with free access of air until all animal and carbonaceous matter has been removed, and a residue of impure calcium phosphate is left), with twice its weight of hydrochloric acid (diluted with four times its volume of water) in a test-tube or larger vessel; the phosphate is dissolved.

$$\underset{\substack{\text{Calcium}\\\text{phosphate}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid}}}{4HCl} = \underset{\substack{\text{Acid calcium}\\\text{phosphate}}}{CaH_4(PO_4)_2} + \underset{\substack{\text{Calcium}\\\text{chloride}}}{2CaCl_2}$$

Dilute the solution with water, boil, filter, and when cold, add excess of ammonia solution; the calcium phosphate, now practically pure (*Calcii Phosphas*, B.P.), is reprecipitated as a light white amorphous powder. After well washing, the precipitate should be dried over a *water-bath* (*see* p. 124), or at a temperature not exceeding 212° F. (100° C.), to prevent undue aggregation of the particles.

$$\underset{\substack{\text{Acid calcium}\\\text{phosphate}}}{CaH_4(PO_4)_2} + \underset{\substack{\text{Calcium}\\\text{chloride}}}{2CaCl_2} + \underset{\text{Ammonia}}{4NH_3} = \underset{\substack{\text{Calcium}\\\text{phosphate}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{Ammonium}\\\text{chloride}}}{4NH_4Cl}$$

Bone-ash or *bone-earth* contains small quantities of calcium carbonate and sulphide. These are decomposed in the above process by the acid, calcium chloride being formed; on boiling the mixture, carbonic anhydride and hydrogen sulphide are evolved. Any carbonaceous or siliceous matter, etc., is removed by filtration. In bones, the calcium phosphate is always accompanied by a small quanity of an allied substance, magnesium phosphate, which is not removed by the process described above. Bone-ash also contains a trace of calcium fluoride, CaF_2.

Calcium phosphate is generally prepared by the interaction of calcium chloride, sodium phosphate, and ammonia, the resulting precipitate being washed with cold water.

A *Water-bath* for the evaporation of liquids or for drying moist solids at temperatures below 212° F. (100° C.), is an iron, tin, or earthenware pan, the mouth of which can be narrowed by iron or tin diaphragms of various sizes, so as to adapt it to the diameters of basins or plates. (*See* fig. 18, p. 73). In the British Pharmacopœia, "when a *water-bath* is directed to be used, it is to be understood that this term refers to an apparatus by means of which water or its vapour, at a temperature not exceeding 212° F. (100° C.), is applied to the outer surface of a vessel containing the substance to be heated, which substance may thus be subjected to a heat near to, but necessarily below, that of 212° F. (100° C.)." Evaporation *in vacuo* is performed by simply placing the vessel of liquid over, or by the side of, a small vessel containing concentrated sulphuric acid or other absorbent of moisture, on the plate of an air-pump, covering with a capacious glass hood or "receiver," and exhausting.

Sodium Phosphate.—Ordinary sodium phosphate, Na_2HPO_4, $12H_2O$ (*Sodii Phosphas*, B.P.), is prepared from calcium phosphate as follows: Mix in a mortar, 3 ounces of ground bone-earth with 1 fluid ounce of sulphuric acid; set aside for twenty-four hours to allow the interaction to take place; add about 3 ounces of water, and put in a warm place for two days, a little warm water being added to make up for that lost by evaporation; stir in another 3 ounces of water, warm the whole for a short time, filter, and wash the residual calcium sulphate on the filter in order to remove adhering acid calcium phosphate; concentrate the *filtrate* (*i.e.*, the liquid which has passed through the filter), to about 3 ounces, and filter again if necessary. To the hot solution, which contains acid calcium phosphate add solution of sodium carbonate (prepared from about 4½ ounces of the crystallized salt) until a precipitate (calcium hydrogen phosphate, $CaHPO_4$) no longer forms, and the liquid is faintly alkaline; filter, evaporate, and set aside to crystallize. The following equations show the two decompositions which occur during the operations :—

$$\underset{\substack{\text{Calcium}\\\text{phosphate}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{Sulphuric}\\\text{acid}}}{2H_2SO_4} = \underset{\substack{\text{Acid calcium}\\\text{phosphate}}}{CaH_4(PO_4)_2} + \underset{\substack{\text{Calcium}\\\text{sulphate}}}{2CaSO_4}$$

$$\underset{\substack{\text{Acid calcium}\\\text{phosphate}}}{CaH_4(PO_4)_2} + \underset{\substack{\text{Sodium}\\\text{carbonate}}}{Na_2CO_3} = \underset{\substack{\text{Sodium}\\\text{phosphate}}}{Na_2HPO_4} + \underset{\text{Water}}{H_2O} + \underset{\substack{\text{Carbonic}\\\text{anhydride}}}{CO_2} + \underset{\substack{\text{Calcium}\\\text{hydrogen}\\\text{phosphate}}}{CaHPO_4}$$

Sodium phosphate crystallizes "in transparent colourless rhombic prisms, terminated by four converging planes, efflorescent, having an alkaline reaction and a saline taste." One part in ten of water constitutes "Solution of Sodium Phosphate," B.P. The crystals effloresce rapidly in the air until nearly half the water has escaped, and a salt is obtained which has a permanent composition represented by the formula, $Na_2HPO_4, 7H_2O$. Another sodium phosphate (sodium dihydrogen phosphate), NaH_2PO_4, H_2O, is obtained by mixing solutions of phosphoric acid and sodium carbonate in the right proportions, evaporating the mixed solution and setting it aside to crystallize.

Calcium Hypochlorite

Experiment 6.—Pass chlorine, generated from black manganese oxide and hydrochloric acid as already described, over damped slaked lime contained in a piece of wide tubing, the outlet end of which is connected with a tube leading into a fume-cupboard. The product is ordinary *bleaching-powder*, a compound of calcium hypochlorite and chloride, mixed with a quantity of unchanged calcium hydroxide. It is commonly called *chloride of lime*, the *Calx Chlorinata* of the British Pharmacopœia, and is one of the most efficient of known disinfectants.

$$\underset{\substack{\text{Black man-}\\\text{ganese oxide}}}{MnO_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid}}}{4HCl} = \underset{\substack{\text{Manganous}\\\text{chloride}}}{MnCl_2} + \underset{\text{Water}}{2H_2O} + \underset{\text{Chlorine}}{Cl_2}$$

$$\underset{\substack{\text{Calcium}\\\text{hydroxide}}}{2Ca(OH)_2} + \underset{\text{Chlorine}}{2Cl_2} = \underset{\text{Water}}{2H_2O} + \underset{\substack{\text{Calcium}\\\text{hypochlorite}}}{CaCl_2O_2} + \underset{\substack{\text{Calcium}\\\text{chloride}}}{CaCl_2}$$

Chlorinated lime exposed to air and moisture, as in disinfecting the atmosphere of sick-rooms, slowly yields hypochlorous acid, $HClO$, calcium carbonate being formed at the same time. Free hypochlorous acid soon breaks up into water, chloric acid, $HClO_3$, and free chlorine. Chloric acid is also unstable, decomposing into oxygen, chlorine, water, and perchloric acid, $HClO_4$. The small quantity of hypochlorous acid diffused through an apartment when bleaching-powder is exposed, thus yields fourteen-fifteenths of its chlorine in the form of chlorine gas.

Constitution of bleaching-powder.—Treated with alcohol, bleaching-powder does not yield its calcium chloride to the solvent; hence the powder is not a mere mixture of calcium chloride and hypochlorite: water, also does not dissolve out first one salt and then the other, but both together, in the molecular proportions of the formula, p. 125. On the other hand, when the aqueous solution is cooled, or evaporated *in vacuo,* crystals are obtained which Kingzett has shown to be nearly pure calcium hypochlorite, the solution containing calcium chloride. While the former fact indicates that the powder is a compound, and not a mere mixture, the latter indicates that it is a feeble compound—an adhesion of molecules of hypochlorite and chloride, as shown in the equation, rather than any closer or more intimate combination of atoms. If it be regarded as a single rather than a double salt, then the following formula (Odling) may be employed, $CaOCl_2$, or $Ca\begin{cases}Cl\\ClO.\end{cases}$

Bleaching-liquor.—Digest chlorinated lime in water, in which the bleaching compound is soluble. Filter from undissolved lime, etc., and test the bleaching powers of the clear liquid by adding a few drops to a decoction of logwood slightly acidulated. When one pound of bleaching-powder is shaken several times during three hours with 1 gallon of distilled water and the liquid is strained, the official Solution of Chlorinated Lime (*Liquor Calcis Chlorinatæ,* B.P.) is obtained.

Experiment 7.—Mix a little powdered wood charcoal with three or four times its weight of gypsum, and heat to redness in a crucible. Some of the calcium sulphate is reduced to sulphide, CaS, with production of carbonic anhydride and carbonic oxide. If the product contains not much less than 50 per cent. of calcium sulphide, it is the official Sulphurated Lime (*Calx Sulphurata*, B.P.).

Official test.—"If 0·8 gramme be mixed with a cold solution of 1·4 grammes of copper sulphate in 50 cubic centimetres of water, and, after the addition of a little hydrochloric acid, the mixture be well stirred and heated to a temperature approaching that of ebullition until all action has ceased, and then filtered, the filtrate should give no red colour with solution of potassium ferrocyanide (presence of a due proportion of sulphide)."

The explanation of the mode of action of this test is as follows:—Cupric sulphate and calcium sulphide interact in the presence of the acid, giving insoluble cupric sulphide and calcium sulphate, thus:—$CuSO_4 + CaS = CuS + CaSO_4$.

On adding up the atomic weights of the constituent elements of crystallized cupric sulphate, 247·86 will be found to be the formula weight; while CaS will similarly represent 71·53 parts. As 247·86 is to 71·53, so (approximately) is 14 to 4. But only half of the sulphurated lime is calcium sulphide; therefore 8 grains of such sulphurated lime will interact with 14 of cupric sulphate. If the 8 grains are below the stated strength, then they will not attack the whole of the 14 grains of cupric salt, and, in that case, potassium ferrocyanide will reveal copper in the filtered liquid.

Calcium Gummate

Calcium Gummate is the only official calcium salt that remains to be noticed. This compound is, in short, *arabin*, the ordinary Gum-Acacia or Gum-Arabic (*Acaciæ Gummi*, B.P.). A solution of gum-arabic in water (*Mucilago Acaciæ*, B.P.) yields a white precipitate of calcium oxalate on the addition of solution of ammonium oxalate; or a piece of gum incinerated in a porcelain crucible yields a calcareous residue, which, when dissolved in a dilute acid, affords characteristic reactions with any of the analytical tests for calcium salts, described further on. In some specimens of gum-arabic a portion of the calcium is displaced by an equivalent quantity of potassium or magnesium. The gummic or arabic radical may be precipitated as opaque gelatinous lead gummate by the addition of a solution of lead subacetate to an aqueous solution of gum. These statements should be verified by experiment.

Tragacanth (*Tragacantha*, B.P.) is a mixture of soluble arabinoid gum and a variety of calcium gum, insoluble in water, termed *bassorin*. With water, a gelatinous mucilage is formed (*Mucilago Tragacanthæ*, B.P.).

Calcium Carbide

Calcium carbide is of interest chiefly on account of the easy method of preparing acetylene which its interaction with water affords. It may be obtained by subjecting an intimate mixture of calcium oxide and carbon to the exceedingly high temperature of the electric furnace. The carbide has the composition CaC_2, and is usually met with as a fused homogeneous black mass, although when quite pure it is colourless and transparent. Water rapidly decomposes it, with the evolution of almost perfectly pure acetylene. Dilute acids behave in the same way as water; concentrated nitric and sulphuric acids attack it but slightly.

Analytical Reactions of Calcium Salts.

1. Add dilute sulphuric acid to a solution of a calcium salt contained in a test-tube or small test-glass; a precipitate of calcium sulphate, $CaSO_4$, is formed if the solution is not too dilute. The calcium is not completely precipitated as sulphate, because this salt, unlike barium sulphate, is quite appreciably soluble in water. The addition of solution of calcium sulphate to a solution of another calcium salt does not produce a precipitate even on standing for some time or on boiling. (Compare the behaviour of barium and of strontium salts).

Solution of Calcium Sulphate.—The official test-liquid termed "Solution of Calcium Sulphate," B.P., is prepared by rubbing calcium sulphate in a mortar with distilled water, and adding more water to form a $1\frac{1}{4}$ per cent. mixture. One ounce of water dissolves about 1 grain of calcium sulphate.

2. Add potassium chromate, K_2CrO_4, to a solution of a calcium salt slightly acidified with acetic acid; no precipitate is produced even on standing or on boiling. (Compare the behaviour of barium and strontium salts.)

These two reactions are most valuable in analysis, as every precipitant of calcium is also a precipitant of barium and of strontium; but in dilute solutions, calcium sulphate and (in presence of acetic acid) potassium chromate are precipitants of barium only.

Other Analytical Reactions.—To separate portions of a solution of a calcium salt, add ammonium carbonate, sodium phosphate, and ammonium oxalate. Precipitates are obtained which correspond in appearance to those produced in the case of a solution of a barium salt; their composition is also analogous, hence their correct formulæ can easily be deduced and equations written to represent the actions which take place. Of the precipitants just mentioned, ammonium oxalate is the one most commonly used as a reagent for calcium salts, in the absence of barium. Calcium oxalate is insoluble in acetic, but soluble in hydrochloric or nitric acids. Calcium compounds impart a reddish colour to the Bunsen flame.

QUESTIONS AND EXERCISES

Write a paragraph on strontium, its natural compounds, chemical relations, technical applications, and tests.—Enumerate some of the common natural compounds of calcium.—Represent by an equation the action of hydrochloric acid on marble.—Why is calcium chloride used as a desiccating agent for gases?—How would you purify Calcium Chloride which has been made from ferruginous marble? Give diagrams.—Write a few lines on the chemistry of the lime-kiln. —What occurs when lime is "slaked"?—To what extent is lime soluble in water (*Liquor Calcis*, B.P.); and in Syrup (*Liquor Calcii Saccharatus*, B.P.)?—Describe the preparation of the official Precipitated Calcium Carbonate (*Calcii Carbonas Præcipitatus*, B.P.); how does it differ from Prepared Chalk (*Creta Præparata*, B.P.)?—How does filter-paper differ from other kinds of paper?—Explain the construction of a "wash-bottle."—Define *decantation*.—State the difference between bone-ash and *Calcii Phosphas*.—How is "bone-earth" purified for use in medicine?—Give equations showing the conversion of Calcium Phosphate into Sodium Phosphate.—Write a short article on the manufacture, composition, and uses of "bleaching-powder" (*Calx Chlorinata*, B.P.).—How may calcium be detected in Gum-Arabic?—State the chemical nature of Tragacanth.—To what extent is calcium sulphate soluble in water?—Barium being absent, what reagents may be used for the detection of calcium? Which is the chief test?

MAGNESIUM: Mg. Atomic Weight, 24·18

Occurrence, etc.—Magnesium is abundant in nature in the form of magnesian or mountain limestone, termed *dolomite* (after Dolomieu, a geologist), a double magnesium and calcium carbonate, in very common use as a building-stone (*e.g.*, the Houses of Parliament and the School of Mines, in London), and *magnesite*, a tolerably pure magnesium carbonate, though too "stony" for direct use in medicine, even if very finely powdered. Magnesium chloride and magnesium sulphate (Epsom salt) occur in the water of many springs, and magnesium salts also occur in sea water and impart to it its bitter taste. A hydrous sulphate, $MgSO_4, H_2O$, termed *kieserite*, occurs near Stassfurt, in Prussia. Metallic magnesium may be obtained from the chloride by strongly heating it with sodium. The metal burns readily in the air, emitting a dazzling light due to the white heat to which the resulting particles of magnesia, MgO, are raised. The chloride to be employed as a source of the metal, is obtained by dissolving the carbonate in hydrochloric acid, adding ammonium chloride, evaporating to dryness, heating the residue in a deep vessel (on the small scale, a large test-tube or flask) until the ammonium chloride is all volatilized, and the magnesium chloride remains as a clear fused liquid. The latter is poured upon a clean earthenware slab. The ammonium chloride is added in order to prevent the interaction of magnesium chloride and water which would otherwise take place in the last stages of the operation, with formation of magnesium oxide (or oxychloride) and hydrochloric acid.

Magnesium Sulphate

Experiment 1.—To a few drops of dilute sulphuric acid in a test-tube, add excess of powdered native magnesium carbonate, *magnesite*, $MgCO_3$, and boil until effervescence ceases and the carbonic anhydride has been completely expelled. The filtered liquid is a solution of magnesium sulphate, crystals of which, *Epsom salt,* $MgSO_4, 7H_2O$ (*Magnesii Sulphas,* B.P.), may be obtained on boiling off most of the water, and setting the concentrated solution aside to cool. This is an ordinary manufacturing process. Instead of magnesite, dolomite may be employed, any iron being removed by evaporating the solution to dryness (after filtering from the calcium sulphate produced), gently igniting to decompose ferrous sulphate, dissolving in water, filtering from ferric oxide, and crystallizing. If neither mineral be at hand, the student may use a little of the ordinary magnesium carbonate used in pharmacy.

$$\underset{\text{“Magnesite”}}{MgCO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid}}}{H_2SO_4} = \underset{\substack{\text{Magnesium}\\\text{sulphate}}}{MgSO_4} + \underset{\text{Water}}{H_2O} + \underset{\substack{\text{Carbonic}\\\text{anhydride}}}{CO_2}$$

Magnesium sulphate crystallizes in large colourless, transparent, rhombic prisms ; but, from concentrated solutions, the crystals are deposited in short, thin needles, a form more convenient for manipulation, solution, and general use in medicine. The crystallized salt loses $6H_2O$ when heated to 300° F. (about 150° C.).

Iron may be detected in magnesium sulphate by adding a solution of chlorinated lime or chlorinated soda to an aqueous solution of the salt; brown ferric hydroxide, $Fe(OH)_3$, is then precipitated. Ammonium hydrosulphide will also give a black precipitate if iron be present.

Effervescent Magnesium Sulphate (*Magnesii Sulphas Effervescens,* B.P.) is magnesium sulphate dried until nearly half its water of crystallization has been removed, and then mixed with citric and tartaric acids, sodium bicarbonate, and sugar.

Magnesium Carbonates

Experiment 2.—To solution of magnesium sulphate add solution of sodium carbonate and boil ; the resulting precipitate is *light* magnesium carbonate (*Magnesii Carbonas Levis,* B.P.), a white, partly amorphous, partly minutely crystalline magnesium hydroxycarbonate, $3MgCO_3, Mg(OH)_2, 4H_2O$. A denser, slightly granular precipitate of similar chemical composition (*Magnesii Carbonas Ponderosus,* B.P.) is obtained by mixing concentrated solutions of the above salts, evaporating to dryness, then removing the sodium sulphate by digesting the residue in hot water, filtering, washing, and drying the precipitate.

$$\underset{\substack{\text{Magnesium}\\\text{sulphate}}}{4MgSO_4} + \underset{\substack{\text{Sodium}\\\text{carbonate}}}{4Na_2CO_3} + \underset{\text{Water}}{5H_2O} = \underset{\substack{\text{Official magnesium}\\\text{carbonate}}}{3MgCO_3,Mg(OH)_2,4H_2O} + \underset{\substack{\text{Sodium}\\\text{sulphate}}}{4Na_2SO_4} + \underset{\substack{\text{Carbonic}\\\text{anhydride}}}{CO_2}$$

The official proportions for the preparation of the light carbonate are 10 parts of magnesium sulphate and 12 of crystals of sodium carbonate, each dissolved in 80 of cold water, the solutions mixed, boiled for 15 minutes, the precipitate collected on a filter, well washed, drained, and dried at a temperature not exceeding 212° F. (100° C.). The heavier carbonate is made with the same proportions of salts, each dissolved in 20 parts instead of 80 of water, the mixture evaporated quite to dryness, and the residue digested in water and washed until all sodium sulphate is removed (until a white precipitate of barium sulphate is no longer formed on the addition of solution of barium chloride or nitrate to a little of the filtrate).

Another Process (*Pattinson's*).—Considerable quantities of magnesium carbonate are prepared by treating dolomite (p. 130) with carbonic anhydride under pressure. The magnesium carbonate dissolves before the calcium carbonate, and is then precipitated from the clear solution by treatment with steam. (Compare next experiment.)

Experiment 3.—Pass carbonic anhydride, generated as described on p. 73, into a mixture of water and magnesium carbonate contained in a test-tube. After some time, separate any undissolved carbonate by filtration; the filtrate contains magnesium carbonate dissolved in carbonic acid. When of a strength of about 10 grains of *official* carbonate in one ounce, such a solution constitutes "Fluid Magnesia" (*Liquor Magnesii Carbonatis,* B.P.). It is possible to obtain a solution containing about 3 per cent. at about 55° F., which is reduced to 2½ per cent. at 70° and to about 2 per cent. at 80°.

The official solution is made from freshly prepared carbonate. The latter is obtained by adding a hot solution of 2 ounces of magnesium sulphate in half a pint of water to one of 2½ ounces of crystals of sodium carbonate in another half-pint of water, boiling the mixture for a short time (to complete decomposition), filtering, thoroughly washing the precipitate, placing the latter in 1 pint of distilled water, and transmitting carbonic anhydride through the liquid (say, at the rate of three or four bubbles per second) for an hour or two, leaving the solution in contact with the gas under pressure of about three atmospheres for twenty-four hours, and, finally, decanting from undissolved carbonate; then, after passing in a little more gas, keeping in a well-closed bottle. Slight pressure is best produced by placing the carbonate and water in a bottle fitted with a cork and tubes as for a wash-bottle (p. 121), conveying the gas by the tube which reaches to the bottom, and allowing excess of gas to flow out by the upper tube, the outlet end of which is continued to the bottom of a small bottle in which mercury, to the depth of about an inch, has been placed. The bottle should be loosely plugged with cotton wool, to prevent loss of metal by spurting during the passage of the gas through it. (Each inch in depth of mercury through which the gas escapes corresponds to about half a pound pressure on every square inch of surface within the apparatus.)

Heat a portion of the solution: hydrous magnesium carbonate, $MgCO_3, 3H_2O$, is precipitated. A salt having the same composition is deposited in crystals by the spontaneous evaporation of the solution. On exposure to cold, the solution sometimes affords large thick crystals ($MgCO_3, 5H_2O$), which, in the air, lose water, become opaque, and then have the composition of those deposited by evaporation ($MgCO_3, 3H_2O$).

Magnesium Oxide. Magnesia

Experiment 1.—Heat light magnesium carbonate in a porcelain crucible over a lamp (or in a larger earthen crucible in a furnace) till it ceases to effervesce on adding a dilute acid to a small portion; the residue is light magnesia, MgO (*Magnesia Levis*, B.P.). The same operation on the heavy carbonate yields heavy magnesia, MgO (*Magnesia Ponderosa*, B.P.). Both are sometimes called calcined magnesia. A given weight of the official light magnesia occupies three and a half times the bulk of the same weight of heavy magnesia.

$$\underset{\text{Official magnesium carbonate}}{3MgCO_3, Mg(OH)_2, 4H_2O} = \underset{\text{Magnesium oxide}}{4MgO} + \underset{\text{Water}}{5H_2O} + \underset{\text{Carbonic anhydride}}{3CO_2}$$

Magnesium oxide becomes hydroxide in water, slowly at

60° F., rapidly at 212° F. A trace only of hydroxide is dissolved. Moisten some magnesia with water, and place the paste on red litmus-paper; the wet spot, after a time, becomes blue, showing that the hydroxide is slightly soluble. The oxide is liable to become hydroxycarbonate on exposure to moist air.

Effervescing Citrate of Magnesia, so-called, is generally a mixture of sodium bicarbonate, citric acid, tartaric acid, sugar, a small quantity of either magnesium carbonate or sulphate, or of both, and flavouring essences.

True magnesium citrate is made by the interaction of calcined magnesia and citric acid: it is said to be frequently prescribed in large doses in France. The formula of magnesium citrate deposited from solution is $Mg_3(C_6H_5O_7)_2$, $14H_2O$.

Analytical Reactions of Magnesium Salts.

1. Add solution of ammonia or of ammonium carbonate to a solution of a magnesium salt (sulphate, for example), and warm the mixture in a test-tube; the precipitation of part only of the magnesium (as hydroxide, $Mg(OH)_2$, or carbonate, $MgCO_3$) occurs. Add now to a small portion of the mixture of precipitate and liquid a considerable excess of solution of ammonium chloride; the precipitate is dissolved.

It is very necessary to note the solubility of magnesium hydroxide and carbonate in solution of ammonium chloride as important analytical separations of magnesium from other metallic radicals depend upon it. In analytical practice, the ammonium chloride should be added before the ammonia or the ammonium carbonate, as it is often easier to prevent precipitation than to redissolve a precipitate once formed.

2. To some of the solution obtained in the preceding reaction, add solution of sodium or ammonium phosphate; a white granular precipitate of ammonium magnesium phosphate, NH_4MgPO_4, is produced.

3. To another portion of the same solution add ammonium arsenate; a white precipitate of ammonium magnesium arsenate, NH_4MgAsO_4, is produced, which is similar in appearance to the corresponding phosphate.

Note.—Barium, strontium, and calcium are also precipitated by alkali-metal phosphates and arsenates. The other precipitants of magnesium are also precipitants of barium, strontium, and calcium. Hence the analyst always removes any barium, strontium, or calcium by an alkali-metal carbonate, as above indicated; sodium phosphate (or ammonium arsenate or phosphate) then becomes a very delicate test for the presence of magnesium. In speaking of magnesium tests, the absence of barium, strontium, and calcium salts is to be understood.

DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF A SALT OF ONE OF THE METALS, BARIUM, STRONTIUM, CALCIUM, MAGNESIUM.

To a portion of the solution add ammonium chloride, ammonia (until the liquid, after shaking, smells of ammonia), and ammonium carbonate.

<table>
<tr><td colspan="3">A white precipitate is produced. Acidulate another portion of the original solution with acetic acid, and add potassium chromate.*</td><td rowspan="4">No precipitate is produced. To the same portion add ammonium phosphate. A white crystalline precipitate produced either at once, or on standing for some time, indicates
Mg</td></tr>
<tr><td rowspan="2">An immediate yellow precipitate indicates
Ba</td><td colspan="2">No immediate precipitate is formed. To another portion of the original solution add calcium sulphate.</td></tr>
<tr><td>A white precipitate, formed on standing for some time, or on boiling, indicates
Sr</td><td>No precipitate even on standing or on boiling, indicates
Ca</td></tr>
<tr><td colspan="3">Confirm Ba, Sr, or Ca by flame-test.</td></tr>
</table>

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[*] Potassium bichromate must not be used in these operations, or a portion of the barium will remain in the liquid and be precipitated along with, or in the place of, the calcium carbonate (*see* p. 115). The potassium chromate used must not contain carbonate, or calcium will be precipitated along with, or in the place of, barium. (The absence of carbonate may be proved by the non-occurrence of effervescence on the addition of hydrochloric acid to a little of the solution of the chromate, previously made hot in a test tube.)

TABLE OF SHORT DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS CONTAINING ANY OR ALL OF THE METALLIC RADICALS HITHERTO CONSIDERED.

To a portion of the solution add ammonium chloride, ammonia (until the liquid, after shaking, smells of ammonia), and ammonium carbonate. Warm and filter.

<table>
<tr>
<td colspan="3"><i>Precipitate.</i>
$BaCO_3$, $SrCO_3$, $CaCO_3$
Dissolve on the filter in dilute nitric acid, evaporate the solution to dryness; digest the residue in a mixture of equal volumes of alcohol and ether; filter.</td>
<td colspan="2"><i>Filtrate.</i>
Add ammonium phosphate, allow to stand for some time, and filter.</td>
</tr>
<tr>
<td colspan="2"><i>Residue</i>
$Ba(NO_3)_2$ and $Sr(NO_3)_2$
Wash with mixture of alcohol and ether, dissolve in water, add dilute acetic acid, and then K_2CrO_4; filter.</td>
<td rowspan="2"><i>Filtrate</i>
Contains
$Ca(NO_3)_2$
Expel the alcohol and ether by gently heating on a water-bath. Dissolve the residue in water, and add
$(NH_4)_2C_2O_4$
A white precipitate indicates
Ca</td>
<td rowspan="2"><i>Precipitate.</i>
White crystalline
NH_4MgPO_4
indicates
Mg</td>
<td rowspan="3"><i>Filtrate.</i>
(<i>a</i>) Boil a portion. A white precipitate indicates Li. Confirm Li by flame-test.
(<i>b</i>) Test for K by the bismuth thiosulphate test (p. 82).
(<i>c</i>) Test for Na by flame-test.
Test for NH_4 in the original solution by boiling with sodium hydroxide. Smell of ammonia indicates
NH_4</td>
</tr>
<tr>
<td><i>Precipitate</i>
Yellow, formed immediately indicates
Ba</td>
<td><i>Filtrate.</i>
Add
$(NH_4)_2CO_3$
till alkaline. A white precipitate indicates
Sr</td>
</tr>
<tr>
<td colspan="3">Confirm Ba, Sr, or Ca by dissolving the $BaCrO_4$, $SrCO_3$, or CaC_2O_4 in HCl, and applying the flame-test.</td>
<td></td>
</tr>
</table>

Note 1.—The analysis of solutions containing the foregoing metals is commenced by the addition of ammonium chloride and ammonia, simply as a precautionary measure, the former compound preventing partial precipitation of magnesium, the latter neutralizing acids. The ammonium carbonate is the barium group precipitant.

Note 2.—In the preceding, and in subsequent tables of analytical processes, the leading precipitants will be found to be ammonium salts. These, being volatile, can be got rid of towards the end of the operations, and thus the detection of potassium and sodium is in no way prevented—an advantage which would be lost if such salts as potassium carbonate or sodium phosphate were the group precipitants employed.

Note on Classification.—The compounds of barium, strontium, calcium, and magnesium have many analogies; their carbonates, phosphates, and arsenates are insoluble in water, which sufficiently distinguishes them from the members of the group of alkali-metals. The solubility of their hydroxides in water marks their connection with the alkali-metals; the slightness of that solubility, diminishing as we advance farther and farther from the alkali-metals (baryta being most and magnesia least soluble in water) points to their connection with the next class of metals, the hydroxides of which are insoluble in water. These considerations must not, however, be over-valued. Though the solubility of their hydroxides places barium nearest and magnesium farthest from the alkali-metals, the solubility of their sulphates gives them the opposite order, magnesium sulphate being most soluble, calcium sulphate next, strontium sulphate third, while barium sulphate is practically insoluble in water. These elements are sometimes spoken of as *the metals of the alkaline earths*.

QUESTIONS AND EXERCISES

Name the natural sources of the various magnesium salts.—Give a process for the preparation of Epsom salt.—Draw diagrams illustrative of the formation of magnesium sulphate from *magnesite* and from *dolomite*.—Show by an equation the process for the preparation of the official Magnesium Carbonate.—What circumstances determine the two different states of aggregation of the official Magnesium Carbonates (*Magnesii Carbonas Ponderosus* and *Magnesii Carbonas Levis*, B.P.)?—What are the relations of *Magnesia Ponderosa*, B.P., and *Magnesia Levis*, B.P., to the official Magnesium Carbonates?—How much denser is the one than the other?—Is magnesia soluble in water?—How is "Fluid Magnesia" prepared?—Mention the effects of heat and cold on "Fluid Magnesia."—Ascertain how much magnesia (MgO) can be obtained from 100 grains of Epsom salt.—Calculate the amount of official Magnesium Carbonate which will yield 100 grains of magnesia.—Can magnesium be detected in presence of barium, strontium, or calcium?—Describe the analysis of an aqueous liquid containing salts of barium, strontium, calcium, and magnesium.—How may magnesium be precipitated from solutions containing ammonium salts?

DISTILLATION

The water with which, in analysis, solution of a salt or dilution of a liquid is effected should be pure. Well- and river-waters are unfit for the purpose, because they contain dissolved salts to the extent of some 20 to 60 grains or more per gallon, derived from the soil through which the water percolates; and rain-water is not infrequently contaminated with the dust and *débris* which fall on the roofs whence it is usually collected. Such water is purified by *distillation,* an operation in which the water is, by boiling, converted into steam, and the steam condensed again to water in a separate vessel, the fixed salts remaining in the vessel in which the water is boiled. On the large scale, the boiling is carried on in metal boilers fitted with a hood or head in which there is a wide lateral channel through which the steam passes; on the small scale, either a common glass flask is employed, into the neck of which a glass tube, bent to an acute angle, is fitted by means of a cork; or a *retort* is used (*a*, fig. 29), a

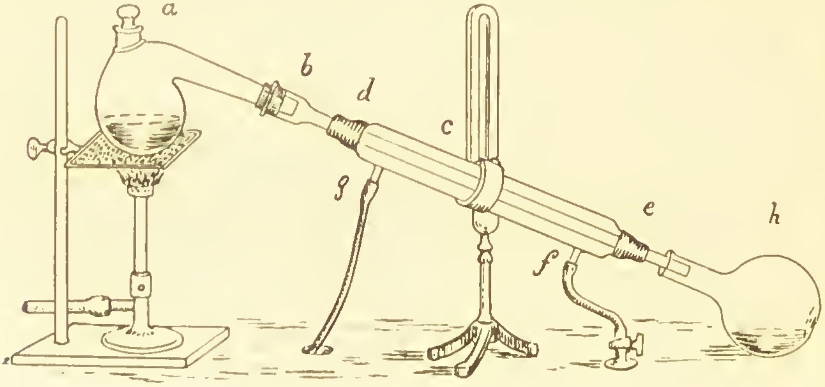

FIG. 29.—Distillation, on a small scale.

species of long-necked flask, bent near the body, by the glass-worker, to an appropriate angle (hence the name *retort*, from *retorqueo*, I bend back). *Condensation* is effected by surrounding the outlet tube through which the steam passes, with cold water. In large stills the steam-tube, or *condensing-worm*, is usually a metal (tin) pipe, coiled into a spiral form for the sake of compactness, and so fixed in a tub that a few inches of one end of the pipe may pass through and closely fit a hole bored near the bottom of the tub. Cold water is kept in contact with the exterior of the pipe, provision being made for a continuous supply to the bottom, while the lighter water, heated by the condensing steam, runs off from the top of the tub. The condenser fitted to a flask or retort may be a simple glass tube of any size, placed within a much wider tube (a common long, narrow lamp-glass may answer for experimental operations), the inner tube being fitted to the wider one by means of bored corks; a stream of water passes in at one end of the enclosed space (the end farthest from the retort), through a small glass tube inserted in the cork, and out at the other end through a similar tube. The common (Liebig's) form of laboratory condenser is a glass tube from one-half to three-fourths of an inch wide and a yard long (*b*, fig. 29), surrounded by an outer tube (*c*, fig. 29) somewhat shorter and about two inches in diameter, and having at each extremity a neck, through which the inner glass tube passes. The junctions of the outer tube with the inner tube are made by means of short, wide indiarubber tubes (*d* and *e*, fig. 29). An inlet (*f*, fig. 29) near the lower part of the outer tube provides for the admission of a current of cold water, conveyed by indiarubber tubing, while an outlet near the top (*g*, fig. 29) allows the escape of heated water into the sink. The inner tube may thus be kept constantly surrounded by cold water, and heated vapours passing through it may be perfectly cooled and condensed, and collected in a receiver (*h*, fig. 29).

In distilling several gallons of water for analytical or medicinal purposes (*Aqua Destillata*, B.P.), the first two or three pints should be rejected, because they are likely to contain traces of ammonia and other volatile impurities.

Pure water is not found in nature; natural water always contains some solid matter in solution, and also dissolved gases. The amount and kind of matter held in solution vary with the source of the water. Water used for distillation should not contain any large amount of impurities, but should be such as is usually supplied to large towns.

Rectification is the process of redistilling a distilled liquid. *Rectified spirit* is spirit of wine which has been thus treated.

Dry or *destructive distillation* is distillation in which the condensed products are directly formed by the decomposing influence of the heat applied to the dry or non-volatile substances in the retort or still, as in the distillation of coal in the manufacture of coal gas.

Exercise.—Write from memory a short description of *distillation.*

At this stage the student is again recommended to read the paragraphs on the general principles of chemical philosophy (pages 40 to 65), and to return to them from time to time, until they are thoroughly comprehended.

ZINC: Zn. Atomic weight, 64·91

Occurrence, etc.—Zinc is tolerably abundant in nature as sulphide, ZnS, *blende*, and carbonate, $ZnCO_3$, *calamine* (from *calamus*, a reed, in allusion to the appearance of the mineral). The ores are roasted to expel sulphur, carbonic anhydride, and some impurities, and the resulting oxide is heated with charcoal, when the metal vaporizes and condenses on cooling. Zinc is a brittle metal, but at a temperature somewhat below 300° F. (148·8° C.) it is malleable, and may be rolled into thin sheets. Above 400° (204·4° C.) it is again brittle, and may then be pulverized. It melts at 773° F. (411·7° C.) and is volatile at a bright red heat. Zinc in exceptionally fine powder ignites spontaneously, especially if damp, or if stored in a warm place.

Uses.—The uses of zinc as a metal are important; alloyed with copper and nickel it yields German silver; with twice its weight of copper it forms brass, and as a coating on iron (the so-called *galvanized* iron) greatly retards the formation of rust. Most of the salts of zinc are prepared, directly or indirectly, from metallic zinc (*Zinc*, B.P.).

Molecular Formula.—Some remarks on this point will be made under Mercury.

Zinc Sulphate

Experiment 1.—Heat zinc (4 parts) with water (20 parts) and sulphuric acid (3 fluid parts) in a test-tube (or larger vessel) until no more hydrogen is evolved; solution of zinc sulphate results. Filter (to separate the particles of lead, carbon, etc., present in ordinary zinc) and concentrate the solution in an evaporating-dish; on cooling, colourless prismatic crystals of Zinc Sulphate, $ZnSO_4,7H_2O$ (*Zinci Sulphas*, B.P.) are deposited.

$$\underset{\text{Zinc}}{Zn} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Zinc sulphate}}{ZnSO_4} + \underset{\text{Hydrogen}}{H_2}$$

The sulphuric acid used in this experiment must be diluted with a considerable quantity of water, as above. Cold concentrated sulphuric acid does not attack zinc.

Note.—Of several methods of preparing hydrogen, the one just described is the most convenient; of the two or three means of preparing zinc sulphate, it is that most commonly employed; and of the many reactions which may be utilized for obtaining a current of electricity, it is one of the most convenient. The apparatus in which the reaction is effected differs according to the requirements of the operator: if the zinc sulphate alone is wanted, an open dish is all that is necessary, the action being accelerated if necessary by heat; if hydrogen is required, a closed vessel and delivery-tube may be used; if a current of electricity is desired, the zinc and sulphuric acid, along with other materials, are placed in glass or earthenware cells, the whole being arranged so as to form a battery.

Purification.—Impure zinc sulphate may be purified in the same manner as impure chloride (*see* next experiment).

Zinc sulphate is isomorphous * with magnesium sulphate, and, like that salt, loses $6H_2O$ when heated to 300° F. (about 150° C.). An old name for it is *white vitriol*.

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* *Isomorphous* bodies (ἴσος, *isos*, equal, and μορφή, *morphé*, form) are those which are similar in the shape of their crystals. This identity in crystalline form is frequently met with amongst substances of analogous composition, such as zinc sulphate, $ZnSO_4,7H_2O$, and magnesium sulphate, $MgSO_4,7H_2O$.

Zinc Chloride

Experiment 2.—Digest zinc in hydrochloric acid mixed with half its bulk of water; the resulting solution contains zinc chloride. Evaporate the liquid till no more steam escapes; Zinc Chloride, $ZnCl_2$, in a state of fusion remains, and, on cooling, is obtained as an opaque white solid (*Zinci Chloridum*, B.P.). It is soluble in water and in alcohol.

$$\underset{\text{Zinc}}{Zn} + \underset{\text{Hydrochloric acid}}{2HCl} = \underset{\text{Zinc chloride}}{ZnCl_2} + \underset{\text{Hydrogen}}{H_2}$$

This reaction is analogous to that described in the preceding experiment. Burnett's deodorizing or disinfecting liquid is a solution of zinc chloride.

Purification of Zinc Chloride or Sulphate.—Zinc sometimes contains traces of iron or lead; and these, like zinc, are dissolved by most acids, with formation of soluble salts: they may be recognised in the solutions by applying the test described on p. 146. Should either be present, a little chlorine water is added to the solution till the odour of chlorine is permanent, and then the whole is well shaken with some zinc hydroxide or the official zinc carbonate. In this way the iron is precipitated as ferric hydroxide, and the lead as peroxide:—

$$\underset{\text{Ferrous chloride}}{{}^*2FeCl_2} + \underset{\text{Chlorine}}{Cl_2} = \underset{\text{Ferric chloride}}{{}^*2FeCl_3}$$

$$\underset{\substack{\text{Ferric}\\ \text{chloride}}}{2FeCl_3} + \underset{\substack{\text{Zinc}\\ \text{hydroxide}}}{3Zn(OH)_2} = \underset{\substack{\text{Ferric}\\ \text{hydroxide}}}{2Fe(OH)_3} + \underset{\substack{\text{Zinc}\\ \text{chloride}}}{3ZnCl_2}$$

$$\underset{\substack{\text{Lead}\\ \text{chloride}}}{PbCl_2} + \underset{\text{Chlorine}}{Cl_2} + \underset{\substack{\text{Zinc}\\ \text{hydroxide}}}{2Zn(OH)_2} = \underset{\substack{\text{Lead}\\ \text{peroxide}}}{PbO_2} + \underset{\substack{\text{Zinc}\\ \text{chloride}}}{2ZnCl_2} + \underset{\text{Water}}{2H_2O}$$

If zinc sulphate is being purified by the above method the action of chlorine on any ferrous sulphate present will result in the formation of ferric chloride as well as ferric sulphate:—

$$6FeSO_4 + 3Cl_2 = 2Fe_2(SO_4)_3 + 2FeCl_3;$$

zinc carbonate will then give zinc chloride as well as sulphate, and thus the whole quantity of zinc sulphate will be slightly contaminated by chloride. On evaporating and crystallizing, however, the zinc chloride will be retained in the mother-liquor. These processes of purification admit of general application.

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* It will be noticed that the atom of iron is represented, in this equation, as both bivalent and trivalent; this will be alluded to when iron comes under consideration.

In the British Pharmacopœia, the possible presence of impurities in the zinc is recognised, and the process of purification just described is incorporated with the process of preparation of *Liquor Zinci Chloridi.*

Liquor Zinci Chloridi, B.P.—1 pound of granulated zinc is placed in a mixture of 44 fluid ounces of hydrochloric acid and 20 of water. The mixture is gently heated until no more gas is evolved. The solution is then boiled and filtered into a bottle; chlorine water is added until the liquid, after shaking, smells of chlorine; about half an ounce or somewhat more of zinc carbonate is shaken up with the solution until a brown precipitate (of ferric hydroxide, or lead peroxide, or both) appears; the whole is then filtered, and the filtrate evaporated to 40 fluid ounces. One fluid ounce contains 366 grains of zinc chloride. If the precipitate obtained on adding ammonia and ammonium hydrosulphide to a little of the solution first produced, is quite white, neither iron nor lead was present in the zinc, and the treatment with chlorine water and zinc carbonate is to be omitted.

Zinc Bromide, $ZnBr_2$, and *Zinc Iodide*, ZnI_2, are included in the United States Pharmacopœia.

Zinc Carbonate

Experiment 3.—To the solution of any given quantity of zinc sulphate in twice its weight of water, add about an equal quantity of sodium carbonate, also dissolved in twice its weight of water, and boil; the resulting white precipitate is Zinc Carbonate (*Zinci Carbonas*, B.P.). It is really a hydroxy-carbonate, capable of being represented as made up of zinc carbonate, $ZnCO_3$ and zinc hydroxide, $Zn(OH)_2$, approximately in the proportion of one molecule of the former and two of the latter, together with a molecule of water ($ZnCO_3$, $2Zn(OH)_2$, H_2O); these proportions, however, vary considerably. It may be washed, drained, and dried in the usual manner. It is used in the arts under the name of *zinc-white.*

$$\underset{\text{Zinc sulphate}}{3ZnSO_4} + \underset{\text{Water}}{3H_2O} + \underset{\text{Sodium carbonate}}{3Na_2CO_3}$$
$$= \underset{\text{Official zinc carbonate}}{ZnCO_3,2Zn(OH)_2,H_2O} + \underset{\text{Carbonic anhydride}}{2CO_2} + \underset{\text{Sodium sulphate}}{3Na_2SO_4}$$

Calamina Præparata is a smooth, pale, pinkish-brown powder, obtained by calcining and powdering native zinc carbonate or *calamine*, and freeing the product from gritty particles by elutriation. *Prepared calamine* is chiefly zinc carbonate with some oxide of iron, etc.

Elutriation (Lat. *elutriatus*, from *elutrio*, I decant; *eluo*, I wash out). This fractional operation consists in decanting off water or other liquid containing lighter and finer particles in suspension, from heavier and coarser particles which have become deposited. The decanted fluid yields a sediment of the fine particles on standing. By allowing varying intervals of time to elapse between the shaking and the decantation, and by using fluids of different specific gravities and different degrees of limpidity or viscidity, substances of different specific gravities, or particles of different degrees of fineness of any one substance, may be separated from each other.

Zinc Acetate

Experiment 4.—Collect on a filter the precipitate obtained in the last experiment, wash with distilled water, and dissolve a portion in concentrated acetic acid; the resulting solution contains zinc acetate, and, on evaporating and setting aside, yields lamellar pearly crystals of zinc acetate, $Zn(C_2H_3O_2)_2$, $3H_2O$ (*Zinci Acetas*, B.P.).

$$\underset{\text{Official zinc carbonate}}{ZnCO_3,2Zn(OH)_2,H_2O} + \underset{\text{Acetic acid}}{6HC_2H_3O_2} = \underset{\text{Zinc acetate}}{3Zn(C_2H_3O_2)_2} + \underset{\text{Water}}{6H_2O} + \underset{\text{Carbonic anhydride}}{CO_2}$$

Zinc Oxide

Experiment 5.—Dry on a water-bath the remainder of the precipitated zinc carbonate obtained in experiment 3, and then heat it in a small crucible until a sample taken out of the crucible does not effervesce on the addition of a dilute acid; the product is Zinc Oxide (*Zinci Oxidum*, B.P.), much used in the form of Ointment (*Unguentum Zinci*, B.P.).

$$\underset{\text{Official zinc carbonate}}{ZnCO_3,2Zn(OH)_2,H_2O} = \underset{\text{Zinc oxide}}{3ZnO} + \underset{\text{Water}}{3H_2O} + \underset{\text{Carbonic anhydride}}{CO_2}$$

Note.—Zinc oxide prepared as above is yellow while hot, and of a very pale yellow or slight buff tint when cold, not actually white like the oxide prepared by the combustion of zinc in air. The preparation of the latter variety, which also occurs in commerce, can only be practically accomplished on the large scale; but the chief features of the action may be observed by heating a piece of zinc on charcoal in the blowpipe-flame (*a*, fig. 30) till it burns; flocks escape, float about in the air, and slowly fall. These were formerly called *Flores Zinci, Lana Philosophica,* or *Nihilum Album.* Zinc oxide slowly absorbs carbonic anhydride and water from moist air, and becomes converted into hydroxycarbonate.

A clear blowpipe-flame consists of two more or less sharply defined portions (*b*, fig. 30), an inner cone, at the apex of which there are hot hydrocarbon gases ready to combine with oxygen, and an outer cone, at the apex of which there is excess of hot oxygen. At the latter point oxidizable metals, etc., are readily oxidized, as in the foregoing experiment, and that part of the flame is therefore termed *the oxidizing flame;* in the inner flame, oxides and other compounds are reduced to the metallic state, hence that part is termed *the reducing flame* (a grain of lead acetate may be employed for illustration). A blowpipe-flame is much altered in character by slight variations in the position of the nozzle of the blowpipe, by the form of the nozzle, by the force with which air is expelled from the blowpipe, and by the character of the jet of gas.

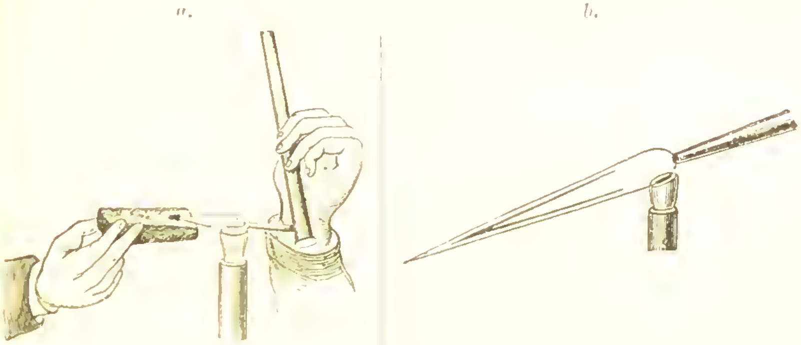

FIG. 30.—The Blowpipe.

Zinc Valerianate

Experiment 6.—Zinc Valerianate, or rather, zinc iso-valerianate, $Zn(C_5H_9O_2)_2$ (*Zinci Valerianas*, B.P.), is prepared by saturating iso-valerianic acid with zinc carbonate or by mixing concentrated solutions of zinc sulphate and sodium iso-valerianate, cooling, separating the white pearly crystalline precipitate, evaporating the solution at 200° F. (93·3° C.) to a small volume, cooling, again separating the lamellar crystals, washing the whole product with a small quantity of cold distilled water, draining, and drying by exposure to air at ordinary temperatures. Zinc iso-valerianate is soluble in ether, alcohol, and hot water. *See* also valerianic acid.

$$\underset{\text{Zinc sulphate}}{ZnSO_4} + \underset{\text{Sodium iso-valerianate}}{2NaC_5H_9O_2} = \underset{\text{Sodium sulphate}}{Na_2SO_4} + \underset{\text{Zinc iso-valerianate}}{Zn(C_5H_9O_2)_2}$$

Zinc Sulphide and *Zinc Hydroxide* are mentioned in subsequent paragraphs. The formula of *Zinc Sulphite* is $ZnSO_3$, $3H_2O$.

Analytical Reactions of Zinc Salts.

1. To a solution of a zinc salt (sulphate, for example), in a test-tube, add a solution of ammonium hydrosulphide, NH_4SH; a white precipitate of zinc sulphide, ZnS, is produced which is insoluble in acetic, but soluble in dilute hydrochloric or sulphuric acid.

Note.—This is the only white sulphide that will be met with. If the zinc salt contains iron or lead as impurities, the precipitate will have a dark appearance, due to admixture with the sulphides of these metals, which are black. Aluminium hydroxide, which is white and may also be precipitated on the addition of ammonium hydrosulphide, is the only substance for which zinc sulphide is likely to be mistaken, or which is likely to be mistaken for zinc sulphide. As will be seen immediately, there are good means of distinguishing these substances from each other.

2. To a solution of a zinc salt add ammonia; a white precipitate of zinc hydroxide, $Zn(OH)_2$, is formed. Add excess

of the reagent; the precipitate is redissolved. This reaction at once distinguishes a zinc salt from an aluminium salt, unless the solution of the latter is very dilute, aluminium hydroxide being almost insoluble in dilute ammonia.

Other Analytical Reactions.—Potassium or sodium hydroxide affords a reaction similar to that just mentioned, the zinc hydroxide redissolving if the alkali does not contain too much carbonate. The solution contains potassium or sodium zincate:—

$$\underset{\substack{\text{Zinc}\\\text{hydroxide}}}{Zn(OH)_2} + \underset{\substack{\text{Caustic}\\\text{potash}}}{2KOH} = \underset{\substack{\text{Potassium}\\\text{zincate}}}{K_2ZnO_2} + \underset{\text{Water}}{2H_2O}$$

(Metallic zinc dissolves in solution of potassium or sodium hydroxide giving hydrogen and potassium or sodium zincate:—$Zn + 2KOH = K_2ZnO_2 + H_2$.) Ammonium carbonate yields a white precipitate of basic zinc carbonate, soluble in excess. Potassium and sodium carbonates give a similar precipitate, which is not redissolved if the mixed solution and precipitate be well boiled to expel carbonic anhydride. Potassium ferrocyanide produces a white precipitate of zinc ferrocyanide, $Zn_2Fe(CN)_6$.

Magnesium sulphate, which is isomorphous with and indistinguishable in appearance from zinc sulphate, does not yield any precipitate when either potassium ferrocyanide or ammonium hydrosulphide is added to its aqueous solution.

Antidotes.—There are no efficient chemical means of counteracting the poisonous effects of zinc. Large doses, fortunately, act as powerful emetics. If vomiting has not occurred, or apparently to an insufficient extent, solution of sodium carbonate (common washing soda), immediately followed by white of egg and demulcents, may be administered, and the stomach then be cleared.

QUESTIONS AND EXERCISES

Give the sources and uses of metallic zinc.—Give a diagram representing the action of zinc on dilute sulphuric acid.—How may solutions of Zinc Chloride or Sulphate be purified from iron salts? Give equations for the reactions.—State the formula of the official Zinc Carbonate, and illustrate by a diagram the reaction which takes place in its production. —Give an equation representing the preparation of Zinc Acetate.—In what respect does Zinc Oxide, resulting from the ignition of the carbonate, differ from that produced during the combustion of the metal?—How is Zinc Iso-valerianate prepared and what are its properties?—Name the more important tests for zinc.—How would you distinguish, chemically, between solutions of Zinc Sulphate and of Alum?—Give reactions distinguishing Zinc Sulphate from Magnesium Sulphate.—Describe the treatment in cases of poisoning by zinc salts.

MANGANESE: Mn. Atomic weight, 54·52

Source.—Manganese is a constituent of many minerals, and is met with in abundance in the south-west of England, in Aberdeenshire, and in most countries of Europe, as black oxide, MnO_2 (Manganese Peroxide, B.P.; *Mangani Dioxidum,* U.S.P.), *pyrolusite* (from πῦρ, *pur,* fire, and λύσις, *lusis,* a loosing or resolving, in allusion to the readiness with which it is split up by heat into a lower oxide and oxygen). This mineral occurs as a steel-grey mass of prismatic crystals, or in black amorphous lumps.

Uses.—Metallic manganese, which may be isolated, amongst other methods, by the action of sodium on manganese fluoride, is used in alloy with iron in the manufacture of some varieties of steel. The black oxide is an important agent in the production of chlorine, and in the preparation of manganates and permanganates, purple glass, and black glaze for earthenware. One soluble salt is included in the United States Pharmacopœia (*Mangani Sulphas,* U.S.P.).

EXPERIMENTS HAVING BOTH SYNTHETICAL AND ANALYTICAL INTEREST

Experiment 1.—Boil some black manganese oxide with concentrated hydrochloric acid in a test-tube or flask, placed in a fume-cupboard, until chlorine is no longer evolved; filter; the filtrate is a solution of manganous chloride, $MnCl_2$. $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$.

This is the reaction commonly employed in the preparation of chlorine. It is also a ready method of preparing a manganous salt for analytical experiments. Coupled with the application of reagents to the filtrate, the reaction is one of those by which a black powder or mineral would be recognised as black manganese oxide. Black manganese oxide also dissolves in *cold* concentrated hydrochloric acid, forming a dark-brown solution which contains a chloride, $MnCl_3$, mixed, probably, with other manganese chlorides.

Experiment 2.—Heat a manganese compound with a grain or two of potassium hydroxide or carbonate and a fragment of potassium nitrate or chlorate on platinum foil in the blowpipe-flame; a green mass containing *potassium manganate*, K_2MnO_4, is formed. Boil the foil and the fused mass in water; the manganate dissolves yielding a green solution which soon changes to purple owing to the formation of *potassium permanganate*, $KMnO_4$. Carefully performed, this is a delicate test for manganese.

This reaction is the one by which potassium permanganate (*Potassii Permanganas*, B.P.) is prepared. *Liquor Potassii Permanganatis*, B.P., is a solution of 87½ grains of potassium permanganate in 1 pint of distilled water. Equations showing the action which occurs in making the salt have already been given in connection with the compounds of potassium (*see* p. 80).

Instead of converting the manganate by ebullition (as described on p. 80), and neutralizing the free alkali by acid, whereby one-third of the manganese is precipitated, chlorine may be passed through the cold solution until the green colour is entirely changed to purple. $2K_2MnO_4 + Cl_2 = 2KMnO_4 + 2KCl$.

Solutions of potassium and sodium manganates and permanganates are in common use as green and purple disinfecting fluids. They act by oxidizing organic matter, the manganic or permanganic radical being reduced and a dark-brown *manganite* formed. For this reason asbestos should be used instead of paper in filtering the solutions.

The changes in colour which the green manganate undergoes when dropped into warm water gave rise to the old name *mineral chameleon*, by which the manganate is still sometimes described.

Experiment 3.—Make a borax bead by heating a fragment of borax on the end of a platinum wire in the blowpipe-flame until a clear transparent globule is obtained. Place a minute particle of a manganese compound, or a drop of a solution of a manganese salt, upon the bead and heat it again in the oxidizing flame. A bead of a pale violet or amethyst tint is produced. (This is useful as an analytical reaction, and it illustrates the use of black manganese oxide in producing common purple-tinted glass.) Expose the bead to the reducing part of the flame (p. 145), the colour disappears. The change is owing to the reduction of the manganic compound to a manganous compound which is nearly colourless (compare ferrous and ferric compounds, p. 163). This action also illustrates the use of black manganese oxide in glass-manufacture. Glass, when first made, is usually of a green tint, owing to the presence of small quantities of ferrous compounds; the addition of the manganese oxide to the materials converts the ferrous into ferric compounds, which have comparatively little colour, it itself being thereby reduced to manganous oxide, which also gives but little colour. If excess of the manganese oxide is added, a purple tint is produced.

Manganese borate is an article of commerce used for the preparation of drying oils and oil varnishes. When moist, it acts as an oxidizing agent with great facility, especially on warming.

Experiment 4.—Through a solution of a manganous salt, acidulated with hydrochloric acid, pass hydrogen sulphide; no precipitate is produced. Add ammonia; the ammonium hydrosulphide thus formed produces a yellowish-pink or flesh-tinted precipitate of manganous sulphide, MnS.

This reaction is characteristic, manganese sulphide being the only flesh-coloured sulphide known. The salt used may be the manganous chloride prepared in experiment 1; but such crude solutions usually give a black precipitate with ammonium hydrosulphide, owing to the presence of iron. *Pure* manganous chloride may be obtained by boiling the impure solution with manganous carbonate; the latter decomposes the ferric chloride, with the production of ferric hydroxide and more manganous chloride, and the evolution of carbonic anhydride.

To the recently precipitated manganous sulphide add acetic acid; it dissolves. This solubility permits of the separation of manganese from nickel, cobalt, and zinc, the sulphides of which are insoluble in dilute acetic acid. To express the fact in another way, manganese is not precipitated by hydrogen sulphide from a solution containing free acetic acid.

Experiment 5.—To a solution of a manganous salt add ammonia; a white precipitate of manganous hydroxide, $Mn(OH)_2$, is produced. Add excess of ammonia; some of the precipitate is dissolved, and may be detected in the quickly filtered solution by the addition of ammonium hydrosulphide. But both precipitate and solution rapidly absorb oxygen, the manganese passing into a more highly oxidized condition, in which it is insoluble in ammonia. Potassium and sodium hydroxides give a similar precipitate *insoluble* in excess. The precipitate rapidly absorbs oxygen, becoming brown, and gradually passing into a higher state of oxidation.

Experiment 6.—To a solution of a manganous salt add dilute nitric acid, and either red lead or lead peroxide, and then boil; a red tint is imparted to the liquid, due to the formation of permanganic acid. If chlorides are present, the manganese, etc., should be separated by means of caustic potash or caustic soda, the precipitate well washed, dissolved in nitric acid, and the oxide then added. (Crum.) Or the chlorides may be got rid of by heating with sulphuric acid until all hydrochloric acid has been expelled (Alcock), and then applying Crum's test. An improvement on Crum's test consists in warming the solution to be tested, which should be free from chloride, with a small quantity of ammonium persulphate to which a drop of a dilute solution of silver nitrate has been added. (H. Marshall.) The purple colour of the solution of permanganic acid is much more easily observed when this method is employed.

COBALT: Co. Atomic weight, 58·56

Sources.—Cobalt occurs sparingly in nature as the arsenide, $CoAs_2$, *tin-white cobalt,* and occasionally as a double arsenide and sulphide, CoAsS, or *cobalt-glance* (from *glanz,* brightness, in allusion to its lustre).

Uses.—Its chief use is in the manufacture of blue glass. A cobalt compound is also the colouring constituent of *smalt* (from *smelt,* a corruption of *melt*), a variety of blue glass reduced to fine powder and used as a pigment by paper-stainers and others, and employed also by laundresses to conceal the yellow tint of imperfectly washed linen.

Cobalt salts, which are mostly reddish and yield pink or red solutions, may be obtained from the oxide, CoO; and the oxide from *zaffre,* a mixture of sand and roasted ore which is chiefly cobalt arsenate. Metallic cobalt is obtained by reducing cobalt oxide (by heating it in a current of hydrogen), or by heating cobalt oxalate in the absence of air.

Analytical Reactions of Cobalt Salts.

1. Pass hydrogen sulphide through an acidulated solution of a cobalt salt (cobalt chloride, $CoCl_2$, or nitrate, $Co(NO_3)_2$, for example); no precipitate is produced. Add solution of ammonia; the ammonium hydrosulphide thus formed causes precipitation of black cobalt sulphide, CoS. (The moist precipitate slowly absorbs oxygen from the air, yielding some cobalt sulphate, $CoSO_4$.)

2. Gradually add solution of ammonia to a solution of a cobalt salt; a blue precipitate of basic salt is produced. Add excess of ammonia; the precipitate is dissolved, yielding a nearly colourless solution, which is rapidly oxidized by the oxygen of the air and becomes brown thereby. Potassium and sodium hydroxides also produce a precipitate of basic salt *insoluble* in excess.

3. Make a borax bead by heating a fragment of borax on the end of a platinum wire in the blowpipe-flame until a clear transparent globule is obtained. Place a minute particle of any cobalt compound, or a drop of a solution of a cobalt salt, upon the bead and heat it again; a blue bead results, in both oxidizing and reducing flames. This is a delicate test for cobalt.

4. To a solution of a salt of cobalt add solution of potassium cyanide until the precipitate which at first forms has entirely redissolved, and further add considerable excess of the cyanide. Then add solution of potassium hydroxide in considerable quantity and an oxidizing agent such as bromine water, and warm. Potassium cobalticyanide, $K_3CoC_6N_6$, is formed in solution but no precipitate is produced. When a nickel solution is similarly treated, the nickel is completely precipitated as black nickelic hydroxide; hence this action affords a means of separating these closely allied metals from each other.

5. To a solution of a cobalt salt add excess of a freshly prepared solution of potassium nitrite in dilute acetic acid. The cobalt is completely precipitated as yellow potassium cobaltic nitrite (Fischer's Salt), $K_3Co(NO_2)_6$. Nickel salts do not give any corresponding reaction.

Invisible Ink.—Many cobalt compounds containing water of crystallization are light red, and in the anhydrous state are more or less blue. Prove this by writing some words on paper with a solution of cobalt chloride sufficiently dilute for the characters to be invisible when dry: hold the sheet before a fire or over a flame; the letters at once become distinctly visible, and of a blue colour. Breathe on the words, or set the sheet aside for some time, the characters become once more invisible, owing to the absorption of moisture. Hence solution of cobalt chloride forms one of the so-called *sympathetic inks*.

NICKEL: Ni. Atomic weight, 58·3

Sources.—The ores of nickel and cobalt are commonly associated in nature. Indeed it is from *speiss*, a nickel arsenio-sulphide obtained in the manufacture of smalt, a pigment of cobalt which has already been mentioned, that much of the nickel of commerce has hitherto been obtained. *Garnierite*, magnesium and nickel silicate, containing no cobalt, is also a valuable source of nickel.

Uses.—Nickel is used in the preparation of the white alloy known as German or nickel silver, and is extensively employed for plating iron.

Nickel salts, which are generally green and yield green solutions, are chiefly made, directly or indirectly, from the metal itself. The latter is obtained by reduction of the oxide by strongly heating it with charcoal.

Analytical Reactions of Nickel Salts.

1. Pass hydrogen sulphide through an acidulated solution of a nickel salt (nickel chloride, $NiCl_2$, nitrate, $Ni(NO_3)_2$, or sulphate, $NiSO_4$); no precipitate is produced. Add ammonia; the ammonium hydrosulphide thus formed causes precipitation of black nickel sulphide, NiS.

Note. — When nickel sulphide is precipitated by the addition of ordinary ammonium hydrosulphide, which contains free sulphur, difficulty is experienced in obtaining a clear liquid on filtering the mixture, owing to the fact that nickel sulphide dissolves to some extent in excess of yellow ammonium hydrosulphide, forming a dark-coloured liquid from which nickel sulphide separates slowly on exposure to the air. From this filtrate, the whole of the nickel can be separated in the form of sulphide by adding excess of acetic acid (which decomposes the yellow ammonium hydrosulphide —the solvent of the nickel sulphide) and filtering again. It can also be separated by driving away the ammonium hydrosulphide by evaporation, and refiltering. In the latter method, some of the nickel sulphide usually undergoes oxidation into nickel sulphate, $NiSO_4$, which passes into solution and must be removed by reprecipitation as sulphide (by adding a few drops of solution of ammonium hydrosulphide and then acidulating with acetic acid), and filtration. It is occasionally practicable to avoid the difficulty by precipitating the nickel sulphide from an ammoniacal solution by means of hydrogen sulphide, or by using freshly-made ammonium hydrosulphide in which nickel sulphide is insoluble.

2. Add solution of ammonia drop by drop to a solution of a nickel salt; a pale-green precipitate of basic salt is produced, especially on boiling the mixture. Add excess of ammonia; the precipitate dissolves, yielding a blue solution. Potassium and sodium hydroxides produce a pale green precipitate of nickel hydroxide, $Ni(OH)_2$, *insoluble* in excess.

3. Nickel salts colour a borax bead reddish-yellow when heated in the oxidizing flame; on heating in the reducing flame, the bead becomes grey and opaque.

4. To a solution of a nickel salt add solution of potassium cyanide; nickel cyanide, $Ni(CN)_2$, is precipitated. Add excess of solution of potassium cyanide; the precipitate is dissolved with formation of potassium nickel cyanide, $K_2Ni(CN)_4$. Then add solution of potassium hydroxide in considerable quantity and bromine water, and warm. The nickel is completely precipitated as black nickelic hydroxide, $Ni(OH)_3$.

QUESTIONS AND EXERCISES

Name the commonest ore of manganese; and give an equation descriptive of its reaction with hydrochloric acid.—Explain the formation of potassium permanganate, giving equations.—How do potassium manganate and permanganate act as disinfectants?—What are the chief tests for manganese?—What are the chief uses of the compounds of cobalt?—How is cobalt analytically distinguished from nickel?—Mention applications of nickel in the arts.—What is the usual colour of nickel salts?

DIRECTIONS FOR APPLYING THE ANALYTICAL REACTIONS DESCRIBED IN THE FOREGOING PARAGRAPHS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS CONTAINING ONE OF THE METALS, ZINC, MANGANESE, COBALT, NICKEL.

First note the colour of the solution:—

Solutions of zinc salts are colourless.

Solutions of manganous salts are colourless or very pale pink.

Solutions of cobalt salts are rose red.

Solutions of nickel salts are green.

Add ammonium chloride, ammonia until the liquid, after shaking, smells of this reagent, and then ammonium hydrosulphide :—*

A white precipitate indicates zinc.

A buff precipitate indicates a manganous salt.

A black precipitate indicates a cobaltous or a nickel salt. To distinguish between cobalt and nickel, add ammonia gradually to a portion of the original solution, without previously adding ammonium chloride. Cobalt gives a blue precipitate, soluble in excess and yielding a brownish solution which gradually darkens. Nickel gives a green precipitate which dissolves in excess yielding a blue solution.

TABLE OF SHORT DIRECTIONS FOR APPLYING THE ANALYTICAL REACTIONS DESCRIBED IN THE FOREGOING PARAGRAPHS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF TWO OR MORE OF THE METALS, ZINC, MANGANESE, COBALT, NICKEL.

If the solution is neutral, acidulate it with acetic acid ; if it is acid, add ammonia until alkaline and then acidulate with acetic acid. Through the acetic acid solution pass hydrogen sulphide until the liquid, after shaking, smells of this gas ; filter.

<table>
<tr><td colspan="2">Precipitate.
Zn, Co, Ni.
Boil with HCl and a little HNO_3, add KOH in excess ; filter.</td><td rowspan="2">Filtrate.
Mn.
Add NH_4OH in excess.
Buff ppt.</td></tr>
<tr><td>Precipitate
Co, Ni.
Dissolve in HCl ; test for Ni as described in Reaction 4 (p. 155). If Ni absent, test solution for Co by borax bead (p. 153) ; if Ni present, filter off nickelic hydroxide, and test filtrate for Co by borax bead.</td><td>Filtrate.
Zn.
Add NH_4SH
white ppt.</td></tr>
</table>

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* Ammonium hydrosulphide added to an ammoniacal solution containing ammonium chloride, is the group-reagent for zinc, manganous, cobaltous, and nickel salts.

ALUMINIUM: Al. Atomic weight, 26·9

Occurrence.—Aluminium is abundant in nature, occurring chiefly as silicate, in clays, slate, marl, basalt, and many other minerals. *Mica* or *laminated talc* consists chiefly of aluminium, iron, magnesium, and potassium silicates. *Spinelle* is magnesium aluminite. *Corundum, sapphire, ruby,* and *amethyst* are almost pure aluminium oxide. *Emery* is an impure aluminium oxide. *Rotten stone* is a soft, friable aluminium silicate containing a little organic matter. *Cryolite* is a double sodium and aluminium fluoride.

The metal aluminium is obtained from the double sodium and aluminium chloride by the action of metallic sodium (the source of the chloride being the mineral *bauxite,* a more or less ferruginous aluminium hydroxide); also by the electrolysis of cryolite. It is readily attacked by various acids, but dilute sulphuric acid only acts upon it slowly.

Aluminium is a remarkably light metal, and in consequence of this property and of the fact that it is practically unchanged by exposure to the air, it is now largely employed for the mountings for opera glasses, etc., and in making cooking utensils for the use of travellers. It readily forms alloys (*see* p. 234) with other metals. One part of aluminium fused with nine of copper gives *aluminium bronze.* *Aluminium steel* is a hard and tenacious alloy of iron with a little aluminium.

Alum (*Alumen,* B.P.), potassium aluminium sulphate, K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$, or ammonium aluminium sulphate, $(NH_4)_2SO_4$, $Al_2(SO_4)_3$, $24H_2O$, may be obtained from alum shale, an aluminous schist (from σχιστός, *schistos,* divided) containing iron pyrites and some bituminous matter, by exposure to air; oxidation in presence of moisture gives rise to the formation of aluminium sulphate, ferrous sulphate, and silica, from the aluminium silicate and iron bisulphide, FeS_2, (iron pyrites) originally present in the shale. The aluminium sulphate and ferrous sulphate are dissolved out of the mass by water, and either potassium or ammonium sulphate or chloride is added; on concentrating the liquid, alum crystallizes out, while the more soluble ferrous sulphate remains in the mother-liquor.

Alum is more frequently prepared by directly decomposing the aluminium silicate in the calcined shale of the coal measures by means of hot sulphuric acid, potassium or ammonium salts being added from time to time, until a solution is obtained which is sufficiently concentrated to crystallize. The liquid, well agitated during cooling, deposits alum in minute crystals termed *alum-flour*, which is afterwards recrystallized.

Alums.—A series of double sulphates, analogous in composition to the alums just mentioned, have been prepared in which sodium may take the place of potassium or ammonium, and iron or chromium may take the place of aluminium. These salts are also called alums; their general formula is M'_2SO_4, $M'''_2(SO_4)_3$, $24H_2O$; and they all crystallize in octahedra. The student should note that iron alum (below) and chrome alum (p. 184) do not contain aluminium. *Ferri et Ammonii Sulphas*, U.S.P., is iron alum, $(NH_4)_2SO_4$, $Fe_2(SO_4)_3$, $24H_2O$.

Ordinary alum commonly occurs in colourless, transparent, octahedral crystals, massed in lumps, which are roughly broken up for trade purposes, but which still exhibit the faces of octahedra. The commercial article sometimes contains potassium sulphate (potash alum), sometimes ammonium sulphate (ammonia alum).

Note.—The aluminium atom is trivalent, and the formula for aluminium chloride is $AlCl_3$. The composition of aluminium sulphate is never represented by means of a formula with a single atom of aluminium, since this would involve writing $Al(SO_4)_{1\frac{1}{2}}$. In order to avoid writing a fraction, the whole formula is doubled, when we get $Al_2(SO_4)_3$.

Experiment.—Prepare alum by heating a small quantity of powdered pipeclay (aluminium silicate) with about twice its weight of sulphuric acid for some time, dissolving the resulting aluminium sulphate and excess of sulphuric acid in water, and adding potassium carbonate to the clear filtered solution until, after well stirring, the excess of acid is neutralized. (If too much carbonate be added, the aluminium hydroxide which is precipitated when the carbonate is first poured in will not be redissolved even on thorough mixing. Perhaps the readiest indication of neutrality in this and similar cases is the presence of *a small quantity* of precipitate after stirring and warming the mixture.) On evaporating the clear solution, crystals of alum are obtained.

Aluminium Sulphate or "*Alum-cake*," $Al_2(SO_4)_3$, $9H_2O$, prepared from natural silicates in the manner just described, is a common article of trade, serving most of the manufacturing purposes for which alum was formerly employed. (*Alumini Sulphas*, U.S.P.)

Dried Alum (*Alumen Exsiccatum*, B.P.) is potassium alum from which the water of crystallization has been expelled by heat. By calculation from the formula, it will be found that alum contains between 45 and 46 per cent. of water. Dried alum rapidly reabsorbs water from the air, and is slowly but completely soluble in water. At temperatures above 400° F. (204·4° C.) ammonium alum is decomposed, water, ammonia, and sulphuric anhydride escaping, and pure aluminium oxide, Al_2O_3, remaining.

Roche alum, or *Rock alum* (Fr. *roche*, rock), is the name of an impure native variety of alum containing iron. The article sold under this name is generally an artificial mixture of common alum with ferric oxide.

Analytical Reactions of Aluminium Salts.

1. To a solution of an aluminium salt (alum, for example, which contains aluminium sulphate) add ammonium hydrosulphide; a white gelatinous precipitate of aluminium hydroxide is produced:—

$$Al_2(SO_4)_3 + 6NH_4SH + 6H_2O = 2Al(OH)_3 + 3(NH_4)_2SO_4 + 6H_2S$$

2. To a solution of alum add ammonia; aluminium hydroxide is precipitated: add excess of ammonia; the precipitate is practically insoluble.

Principle of Dyeing by help of Mordants.—Precipitated aluminium hydroxide has great affinity for vegetable colouring-matters, and also for the fibre of cloth. Repeat experiment 2, but before adding the ammonia, introduce into the test-tube some decoction of logwood, solution of cochineal, or other solution of an animal or vegetable colouring-matter. Now add the reagent and set the tube aside for the precipitate to settle; the latter takes down with it all the colouring-matter. In dye works, the undyed fabrics are treated with solutions of aluminium acetate in such a manner as to deposit aluminium hydroxide within their fibres, and are then passed through the colouring solutions, from which the hydroxide abstracts colouring-matter. Some other metallic hydroxides, notably those of tin and iron, resemble aluminium hydroxide in this respect; they are termed *mordants* (from *mordens*, biting); the substances they form with colouring-matters are called *lakes*.

3. To a solution of alum add solution of potassium hydroxide; aluminium hydroxide is precipitated. Add excess of the reagent, and agitate; the precipitate dissolves.

Aluminium hydroxide may be precipitated from this solution by neutralizing the potassium hydroxide with hydrochloric acid, and adding ammonia until, after shaking, the mixture smells of ammonia; or by adding a sufficient quantity of solution of ammonium chloride to the alkaline liquid, and boiling until ammonia is no longer evolved.

4. To a solution of alum add solution of potassium or sodium carbonate. A precipitate of aluminium hydroxide is produced, and carbonic anhydride escapes:—

$$Al_2(SO_4)_3 + 3K_2CO_3 + 3H_2O = 2Al(OH)_3 + 3K_2SO_4 + 3CO_2$$

QUESTIONS AND EXERCISES

Enumerate the chief natural compounds of aluminium?—Write down a formula which will represent either of the alums.—Which alum is official, and commonly employed in the arts?—State the source and explain the formation of alum.—What is the crystalline form of alum?—Calculate how much dried alum is theoretically producible from 100 pounds of potassium alum. *Ans.*, 54 lb. 7 oz.—Show that ordinary ammonium alum is capable of yielding 11·269 per cent. of aluminium oxide.—Why are aluminium compounds used in dyeing?—How are aluminium salts analytically distinguished from zinc salts?

IRON : Fe. Atomic weight, 55·6

Sources.—Compounds of iron are abundant in nature. *Magnetic Iron Ore*, or *Loadstone* (*Lodestone* or *Leadstone*, from the Saxon *lædan*, to lead, in allusion to its use, or rather, to the use of magnets made from it, in navigation), Fe_3O_4, is the chief ore from which Swedish iron is made. Much of the

Russian iron is made from *Specular Iron Ore* (from *speculum*, a mirror, in allusion to the lustrous nature of the crystals of this mineral); this and *Red Hæmatite* (from *αἷμα, haima*, blood, so named from the colour of its streak), an ore raised in Lancashire, are composed of ferric oxide, Fe_2O_3. *Brown Hæmatite*, an oxyhydroxide, $Fe_2O(OH)_4$, is the source of much of the French iron. *Needle iron ore*, or *göthite*, is also an oxyhydroxide, $FeO(OH)$. *Spathic Iron Ore* (from *spatha*, a slice, in allusion to the lamellar structure of the ore) is ferrous carbonate, $FeCO_3$. An impure ferrous carbonate forms the *Clay Ironstone*, whence most of the English iron is derived. The chief Scotch ore is also an impure carbonate, containing much bituminous matter: it is known as *Black Band*. *Iron Pyrites* (from *πῦρ, pur*, fire, in allusion to the production of sparks when sharply struck), FeS_2, is a yellow, lustrous mineral, now largely employed as a source of sulphur. As met with in coal, it is commonly termed *coal brasses*. Ferrous bicarbonate, chloride, and sulphate, sometimes occur in springs, the waters of which are hence termed *chalybeate* (*chalybs*, steel).

Manufacture of Iron.—The manufacture of iron from its ores is carried on as a continuous process by means of the *blast-furnace*, a high structure built with fire-bricks. Most manufacturers employ a mixture of ores—the oxide ores simply in the condition in which they are mined, and some other ores after the preliminary operation of *roasting*, or strongly heating in air, to convert them into oxide. The mixed ores, along with coal and limestone, are fed into the top of the blast-furnace, while a current of heated air, forced in at the bottom under considerable pressure, causes the coal to burn rapidly, and thereby maintains a very high temperature inside the furnace. In the course of their passage down from the top, the iron oxides give up their oxygen to form carbonic anhydride, and the reduced iron trickles down and collects at the bottom of the furnace. On its way down, the melted metal is protected from the oxidizing action of the hot-air blast by the *slag*, a fusible glassy substance which is produced by the interaction of the limestone with the sand and clay present as impurities in the ores. The fused slag collects in a layer which lies on the top of the melted iron and is occasionally drawn off. The iron is also drawn off from time to time, and is allowed to flow into narrow branched gutters moulded in sand, where it cools and solidifies, and is afterwards broken up into fragments which constitute *pig-iron*—the form in which *cast-iron* is met with in commerce.

The cast-iron thus produced may be converted into *wrought-iron* by burning out the 4 or 5 per cent. of carbon, silicon, and other impurities present, by oxidation in a furnace—an operation termed *puddling*. *Steel* is iron containing from 1 to 2 per cent. of carbon. It is now made by the Bessemer process, which consists in burning out from cast-iron the variable amount of carbon it contains, and then adding melted iron containing a known proportion of carbon. The official iron (*Ferrum*, B.P.) is "annealed iron wire, having a diameter of about 0·005 inch (0·1 millimetre) (about No. 35 wire gauge), or wrought-iron nails, free from oxide": these being forms in which iron is conveniently employed for conversion into its compounds. In the form of a fine powder, metallic iron is employed as a medicine (*see* p. 177).

Properties.—The specific gravity of pure iron is 7·844; of the best bar iron 7·7. Its colour is bluish white or grey. Bar iron requires the highest heat of a wind-furnace for fusion, but below that temperature it assumes a pasty consistence, and in that state two pieces may be joined or *welded* (Germ. *wellen*, to join) by the pressure of blows from a hammer. A little sand thrown upon the hot metal facilitates this operation by forming with the superficial coating of oxide of iron a fusible slag, which is dispersed by the blows: the purely metallic surfaces are thus better enabled to come into thorough contact and enter into perfect union. Iron is highly ductile, and of all common metals possesses the greatest amount of tenacity. At a high temperature it burns in the air, forming black magnetic oxide. Ordinary *iron rust* is chiefly brown ferric hydroxide or oxyhydroxide, with a little ferrous oxide and carbonate; it is produced by action of the moisture and carbonic anhydride of the air and subsequent oxidation. Steam passed over iron heated to redness yields hydrogen and magnetic oxide of iron.

Quantivalence of Iron. Ferrous and Ferric Salts.—In its union with other elements and with radicals, to form salts, iron exhibits the property of combining with these in two proportions so as to give rise to two distinct sets of salts. In one of these sets, iron appears as a bivalent metal, the formula of the chloride being $FeCl_2$, that of the sulphate,

$FeSO_4$, etc. In the other set iron is trivalent, the formulæ of the chloride and sulphate being $FeCl_3$ and $Fe_2(SO_4)_3$ respectively. These two sets of salts are regarded as related to the two basic oxides of iron, FeO and Fe_2O_3 (the place of the oxygen of the basic oxides being taken by acid radical), and they are known as *ferrous* and *ferric* salts respectively. Thus the "lower" chloride, $FeCl_2$ (or chloride containing the smaller proportion of chlorine) is ferrous chloride, while the "higher" chloride, $FeCl_3$ (or chloride containing the larger proportion of chlorine), is ferric chloride. When the analytical reactions of iron salts come to be studied, it will be found that those of the ferrous and ferric salts are quite different from each other and enable the student to ascertain in which of the two forms of combination the iron is present. This feature of forming two separate sets of salts is not peculiar to iron, but is met with in the cases of copper, mercury, and various other metals. The terminations *ous* and *ic* are employed in these cases in a consistent manner, the former always denoting the compound containing the smaller, and the latter that containing the larger proportion of oxygen (in the case of the basic oxides) and of acid radical (in the case of the salts).

FERROUS SALTS

Ferrous Sulphate. Iron Sulphate

Experiment 1.—Place iron (small tacks) in dilute sulphuric acid, accelerating the action by heat until effervescence ceases.

$$\underset{\text{Iron}}{Fe} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Ferrous sulphate}}{FeSO_4} + \underset{\text{Hydrogen}}{H_2}$$

The solution contains ferrous sulphate, and will yield crystals of that substance, $FeSO_4, 7H_2O$, (*Ferri Sulphas*, B.P.) on cooling or on further evaporation; or if the hot concentrated solution be poured into alcohol, the mixture being well stirred, the sulphate is at once thrown down in minute crystals (*Ferri Sulphas Granulatus*, U.S.P.). At a temperature of 212° F. (100° C.) ferrous sulphate loses six-sevenths of its water, and becomes *Ferri Sulphas Exsiccatus*, B.P.

Other Sources of Ferrous Sulphate.—In the laboratory, ferrous sulphate is often obtained as a by-product in making hydrogen sulphide (p. 102). In the manufacture of alum it occurs as a by-product in the decomposition of the aluminous shale, as already noticed (p. 157).

A two per cent. solution of ferrous sulphate in distilled water constitutes "Solution of Ferrous Sulphate," B.P. "The solution should be recently prepared," because of its liability to absorb oxygen with formation of ferric oxysulphate (*see* below).

Notes.—Ferrous sulphate was formerly termed *green vitriol.* Vitriol (from *vitrum*, glass) was originally the name of any transparent crystalline substance: it was afterwards restricted to the sulphates of zinc, iron, and copper, which were, and still are occasionally, known as white, green, and blue vitriol respectively. *Copperas* (probably originally *Copper-rust*, a term applied to verdigris and other green incrustations of copper) is another name for this iron sulphate, sometimes distinguished as *green copperas*, copper sulphate being blue copperas. Exsiccated ferrous sulphate is a constituent of *Pilula Aloes et Ferri*, B.P. Ferrous sulphate forms a light green double salt with ammonium sulphate (ammonium ferrous sulphate, $(NH_4)_2SO_4$, $FeSO_4$, $6H_2O$).

Ferrous sulphate, when exposed to the air, gradually becomes brown through absorption of oxygen, ferric oxysulphate, $Fe_2O(SO_4)_2$, being formed. The latter is not completely dissolved but is decomposed by water, with the formation of a still lower insoluble oxysalt ($Fe_4O_5SO_4$), and soluble ferric sulphate: $5Fe_2O(SO_4)_2 = Fe_4O_5SO_4 + 3Fe_2(SO_4)_3$.

Iron heated with undiluted sulphuric acid yields sulphurous anhydride and ferrous sulphate:—

$$Fe + 2H_2SO_4 = FeSO_4 + SO_2 + 2H_2O$$

Ferrous Carbonate. Iron Carbonate

Experiment 2.—To a boiling solution of ferrous sulphate, in a test-tube, add a solution of ammonium carbonate, $(NH_4)_2CO_3$, which has been prepared with recently boiled hot water; a white precipitate of ferrous carbonate, $FeCO_3$, is produced which rapidly becomes light-green, bluish-green, and on standing for some time, reddish-brown, owing to absorption of oxygen; carbonic anhydride is evolved, and ferric oxyhydroxide is formed.

$$\underset{\text{Ferrous sulphate}}{FeSO_4} + \underset{\text{Ammonium carbonate}}{(NH_4)_2CO_3} = \underset{\text{Ferrous carbonate}}{FeCO_3} + \underset{\text{Ammonium sulphate}}{(NH_4)_2SO_4}$$

Saccharated Iron Carbonate.—The above precipitate of ferrous carbonate, rapidly washed with hot well-boiled distilled water, and then mixed with sugar and quickly dried—all possible precautions being taken to avoid prolonged exposure to air—forms saccharated iron carbonate (*Ferri Carbonas Saccharatus*, B.P.). The official proportions are two ounces of ferrous sulphate and one ounce and a quarter of "ammonium carbonate," each dissolved in half a gallon of hot water. The solutions are mixed and set aside in a deep, well-covered vessel, the supernatant liquid is poured off when the precipitate has subsided, the vessel is again filled up with boiling water, the liquid once more poured away, the precipitate transferred to a calico filter, drained, gently pressed, and, while still somewhat moist, rubbed in a mortar with one ounce of sugar, and finally dried over a water-bath. This is probably a *mixture* of ferrous carbonate, etc., with sugar; a *compound* known as *iron sucrate*, containing about 48·5 per cent. of iron, is obtained by pouring a solution of cane-sugar and ferric chloride into a slight excess of caustic soda; a reddish-brown crystalline precipitate is produced. *Iron maltosate* is an analogous compound.

Notes.—The red powder formerly termed Carbonate or Subcarbonate of Iron (*Ferri Carbonas* or *Ferri Subcarbonas*) was ferrous carbonate washed and dried with free exposure to air, the product thus, by the absorption of oxygen and the elements of water, and the elimination of carbonic anhydride, becoming ferric oxyhydroxide, a compound which will come under notice subsequently. Ferrous carbonate is said to be more easily dissolved in the stomach than any other iron preparation. It is so easily oxidized, that it must be washed with water free from dissolved air, and then mixed with the sugar (which protects it from oxidation) as quickly as possible. In making the official compound mixture of iron (*Mistura Ferri Composita*, B.P.), "Griffith's mixture," the prepared ingredients, including the potassium carbonate, should be placed in a bottle of the required size, space being left for the crystals or solution of ferrous sulphate, which should be added last, the bottle immediately filled up with the rose-water and securely corked; the minimum of oxidation is thus ensured. The proportions ordered in the official mixture are twice the formula weight of potassium carbonate for once that of ferrous sulphate; hence, as the ferrous carbonate decomposes, the carbonic anhydride produced does not necessarily escape, but converts the potassium carbonate into bicarbonate. *Pilula Ferri*, B.P., *Iron Pill* or "Blaud's Pill," is prepared with exsiccated ferrous sulphate and exsiccated sodium carbonate.

$$FeSO_4 + Na_2CO_3 = FeCO_3 + Na_2SO_4$$

Ferrous Arsenate. Iron Arsenate

See under Arsenium (p. 194).

Ferrous Phosphate. Iron Phosphate

Experiment 3.—To a hot solution of ferrous sulphate in a test-tube, add a hot solution of sodium phosphate and a small quantity of a solution of sodium bicarbonate; ferrous phosphate, $Fe_3(PO_4)_2$, is precipitated. *Ferri Phosphas*, B.P., contains not less than 47 per cent. of hydrous ferrous phosphate, $Fe_3(PO_4)_2, 8H_2O$.

$$\underset{\text{Ferrous sulphate}}{3FeSO_4} + \underset{\text{Sodium phosphate}}{2Na_2HPO_4} + \underset{\text{Sodium bicarbonate}}{2NaHCO_3} =$$

$$\underset{\text{Ferrous phosphate}}{Fe_3(PO_4)_2} + \underset{\text{Sodium sulphate}}{3Na_2SO_4} + \underset{\text{Water}}{2H_2O} + \underset{\text{Carbonic anhydride}}{2CO_2}$$

Officially, solutions of 3 ounces of ferrous sulphate in 30 of hot water, and $2\frac{3}{4}$ ounces of sodium phosphate in 30 of hot water, together with $\frac{3}{4}$ ounce of sodium bicarbonate dissolved in a little water, are well mixed, and the mixture is filtered; the precipitate is thoroughly washed with hot water, and, to prevent oxidation as much as possible, dried at a temperature not exceeding 120° F. (48·8° C.). These proportions will be found to accord fairly with the weights of the crystallized salts required for the foregoing equation. $3(FeSO_4, 7H_2O) = 828{\cdot}3$; $2(Na_2HPO_4, 12H_2O) = 711{\cdot}28$; $2(NaHCO_3) = 166{\cdot}86$.

The addition of the sodium bicarbonate is to ensure the absence of free sulphuric acid from the solution. Sulphuric acid dissolves ferrous phosphate, and it is impossible to prevent the liberation of some sulphuric acid, if only the ferrous sulphate and sodium phosphate be employed without the sodium bicarbonate. Ferrous phosphate is white but soon becomes oxidized and is then slate-blue. Two syrups containing ferrous phosphate are official. *Syrupus Ferri Phosphatis*, B.P., is prepared by dissolving iron wire in concentrated phosphoric acid, and adding syrup; and *Syrupus Ferri Phosphatis cum Quinina et Strychnina*, B.P., in the same manner, quinine sulphate and strychnine being added before the syrup.

Ferrous Sulphide. Iron Sulphide

Experiment 4.—Mix sulphur in a test-tube with about twice its weight of iron filings and strongly heat the mixture in the Bunsen flame (or heat in an earthen crucible in a furnace); ferrous sulphide, FeS, is formed. When the product is cold, add water to a small portion of it, and then a few drops of sulphuric acid; hydrogen sulphide, H_2S, recognisable by its odour, is evolved. $FeS + H_2SO_4 = FeSO_4 + H_2S$.

Sticks of sulphur pressed against a white-hot bar of cast-iron give a pure form of ferrous sulphide. Or melted sulphur may be poured into a crucible full of red-hot iron nails, when a quantity of fluid ferrous sulphide is at once formed and may be poured out on a slab.

Hydrous Ferrous Chloride. Iron Chloride

Experiment 5.—Digest iron tacks or wire, in a test-tube, in hydrochloric acid; hydrogen escapes, and the solution on cooling, or on evaporation and cooling, deposits crystallized ferrous chloride, $FeCl_2, 4H_2O$.

Anhydrous Ferrous Chloride.—See p. 169.

Ferrous Iodide. Iron Iodide

Experiment 6.—Place a piece of iodine, about the size of a pea, in a test-tube, with a small quantity of water, and add a few iron filings, or small nails, or some iron wire. On gently warming, or merely shaking if longer time be allowed, the iodine disappears, and on filtering, a clear light-green solution of ferrous iodide, FeI_2, is obtained. On evaporation, the solid iodide remains.

Solid ferrous iodide contains about 18 per cent. of water of crystallization and a little iron oxide. It is deliquescent and liable to absorb oxygen from the air with formation of insoluble ferric oxyiodide or hydroxyiodide. Ferrous iodide thus oxidized may be purified by re-solution in water, addition of a little more iodine and some iron, warming, filtering, and evaporating as before. Syrup of ferrous iodide (*Syrupus Ferri Iodidi*, B.P.) has already been described on p. 25. Syrup of ferrous iodide which has become brown may usually be restored by immersing the bottle in a water-bath and slowly warming.

Ferrous Bromide, $FeBr_2$, occasionally used in medicine, may be made in a similar way. Its solution in water or syrup is light green.

FERRIC SALTS

Anhydrous Ferric Chloride. (Iron Perchloride)*

Experiment 7.—Pass chlorine (generated from black manganese oxide and hydrochloric acid in a flask) through concentrated sulphuric acid contained in a small wash-bottle (to dry the gas) and then, by means of a glass tube, to the bottom of a test-tube containing twenty or thirty small iron tacks (or a flask containing two or three ounces of them—*see* fig. 31),

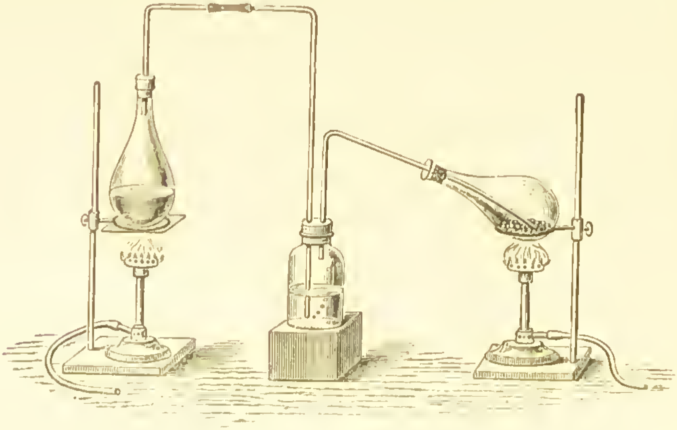

FIG. 31.—Preparation of Anhydrous Ferric Chloride.

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* The prefix *per* (and *hyper*) used here and elsewhere is from *ὑπὲρ*, *hyper*, over or above, and in this case, indicates the higher chloride of iron; that is, iron perchloride is the iron chloride which contains the larger proportion of chlorine.

the latter being kept hot by a gas-flame; ferric chloride (or iron perchloride), $FeCl_3$, is formed and condenses in the upper part of the tube or flask as a mass of small, dark, iridescent crystals. When a tolerably thick crust of the salt is formed, break off the part of the glass containing it, being careful that the remaining corroded tacks are excluded, and place it in ten to twenty times its weight of water: the resulting solution, poured off from any pieces of glass, is a nearly neutral solution of ferric chloride, and may be employed for analytical reactions.

Precaution.—The above experiment must be conducted in the open air, or in a fume-cupboard.

Anhydrous Ferrous Chloride.—In breaking up the vessel, scaly crystals of this substance, $FeCl_2$, of a light-buff colour, will be observed adhering to the nails.

Note.—Solution of ferric chloride gives off some hydrochloric acid on boiling, while a darker-coloured solution of ferric oxychloride remains.

Solution of Ferric Chloride

Experiment 8.—Through a portion of the solution of ferrous chloride prepared in experiment 5, pass chlorine gas; the ferrous chloride is converted into *ferric chloride.* The excess of chlorine dissolved by the liquid in this experiment may be removed by ebullition; but the ferric chloride is liable to be slightly decomposed. (*See* above.) The free chlorine is better carried off by passing a current of air through the liquid for some time.

Strong Solution of Ferric Chloride

Experiment 9.—To a portion of the solution of ferrous chloride, prepared in experiment 5, add a little hydrochloric acid; heat the liquid, and drop in nitric acid until the black colour at first produced, disappears; the resulting reddish-brown liquid is a solution of ferric chloride.

$$\underset{\substack{\text{Ferrous}\\\text{chloride}}}{3FeCl_2} + \underset{\substack{\text{Nitric}\\\text{acid}}}{HNO_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid}}}{3HCl} = \underset{\substack{\text{Ferric}\\\text{chloride}}}{3FeCl_3} + \underset{\substack{\text{Nitric}\\\text{oxide}}}{NO} + \underset{\text{Water}}{2H_2O}$$

The black substance is a compound produced by the interaction of nitric oxide, NO, with some ferrous salt; its composition is $2FeSO_4 + NO$; it is decomposed by heat.

This is the process for producing *Liquor Ferri Perchloridi Fortis*, B.P., 4 ounces of iron wire, 20½ fluid ounces of hydrochloric acid, 1½ of nitric acid, and sufficient water being employed, and the product boiled down to 17½ fluid ounces. Practically it is impossible so to apportion the acids that the resulting solution shall be free from excess of acid, and shall not contain either ferrous salt or ferric nitrate. For most medicinal purposes, however, solution of ferric chloride containing hydrochloric acid is said to be unobjectionable. On the large scale some time may be saved by adopting the official plan of adding the acid solution of ferrous chloride to the nitric acid.

Diluted to four times its volume with water, this strong solution gives *Liquor Ferri Perchloridi*, B.P.—or 1 volume with 1 of alcohol, and sufficient water to produce 4 volumes, gives *Tinctura Ferri Perchloridi*, B.P.

Note.—The alcohol in the latter preparation does not act either as a special solvent or as a preservative—the offices usually performed by alcohol in B.P. preparations—and, as a matter of fact, unless the liquid contain excess of acid, it decomposes the ferric chloride and causes the formation of an insoluble ferric oxychloride. Even if the tincture be acid, it slowly loses colour, ferrous chloride and ethereal compounds containing chlorine being formed. The *Liquor*, which is similar in strength, is not liable to such decomposition and such variation in characters.

Solution of Ferric Chloride, when evaporated, yields a mass of yellow crystals having the composition $FeCl_3, 6H_2O$, or, under other conditions, red crystals represented by the formula $2FeCl_3, 5H_2O$.

Ferric Sulphate (formerly called Iron Persulphate)*

Experiment 10.—Dissolve about three-quarters of an ounce of ferrous sulphate and a sixth of this weight of sulphuric acid in an ounce and a half of water in an evaporating-dish, heating the mixture and dropping in nitric acid until the black colour at first produced, disappears. The resulting liquid, when made of a certain prescribed strength, is solution of ferric sulphate (*Liquor Ferri Persulphatis*, B.P.), a heavy, dark-red liquid.

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* The name persulphate cannot now be applied consistently to this substance. The *persulphates* form a definite series of salts derived from persulphuric acid, $H_2S_2O_8$ (*see* Index). Ferric sulphate is simply the sulphate corresponding to the higher basic oxide of iron—ferric oxide, Fe_2O_3, formerly called sesquioxide, and sometimes peroxide, of iron.

$$\underset{\substack{\text{Ferrous}\\\text{sulphate}}}{6FeSO_4} + \underset{\substack{\text{Sulphuric}\\\text{acid}}}{3H_2SO_4} + \underset{\substack{\text{Nitric}\\\text{acid}}}{2HNO_3} = \underset{\substack{\text{Ferric}\\\text{sulphate}}}{3Fe_2(SO_4)_3} + \underset{\substack{\text{Nitric}\\\text{oxide}}}{2NO} + \underset{\text{Water}}{4H_2O}$$

The black colour, as in experiment 9, is due to the formation of a compound by the interaction of ferrous salt with nitric oxide.

The official solution of ferric sulphate is made by adding 6 fluid drachms of sulphuric acid to half a pint of water, warming, dissolving 8 ounces of crystallized ferrous sulphate in the liquid, then pouring it into nitric acid (6 fluid drachms or rather more) slightly diluted, until ruddy nitrous vapours are no longer produced, and the liquid has acquired a reddish colour. The whole should measure 11 fluid ounces, being diluted or further evaporated, as the case may be, to this volume.

Ferric Hydroxide and Ferric Oxyhydroxide

Experiment 11.—Pour a portion of the solution of ferric sulphate into excess of solution of caustic soda; ferric hydroxide, $Fe(OH)_3$, is precipitated. Wash the precipitate by decantation or on a filter, and dry it on a water-bath; ferric oxyhydroxide, $FeO(OH)$, remains.

$$\underset{\substack{\text{Ferric}\\\text{sulphate}}}{Fe_2(SO_4)_3} + \underset{\substack{\text{Caustic}\\\text{soda}}}{6NaOH} = \underset{\substack{\text{Ferric}\\\text{hydroxide}}}{2Fe(OH)_3} + \underset{\substack{\text{Sodium}\\\text{sulphate}}}{3Na_2SO_4}$$

$$\underset{\text{Ferric hydroxide}}{Fe(OH)_3} = \underset{\text{Ferric oxyhydroxide}}{FeO(OH)} + \underset{\text{Water}}{H_2O}$$

Either of the other alkalies (caustic potash or ammonia) would produce a similar reaction.

Ferric hydroxide is an antidote in cases of arsenical poisoning, if administered directly after the poison has been taken. It converts the soluble arsenious acid, H_3AsO_3, into insoluble ferrous arsenate:—

$$4Fe(OH)_3 + 2H_3AsO_3 = Fe_3(AsO_4)_2 + 8H_2O + Fe(OH)_2$$

Ferric hydroxide becomes converted into oxyhydroxide, when dried, and has then less action on the arsenious acid. Even the moist recently prepared hydroxide loses much of its action as soon as it has changed into one of the oxyhydroxides, $Fe_4O_3(OH)_6$, a change which will occur though the hydroxide be kept under water (W. Procter, jun.). According to T. and H. Smith, this decomposition occurs gradually, but in an increasing ratio; so that after four months the power of the moist mass is reduced to one-half, and after five months to one-fourth.

A ferric oxycarbhydroxide, $Fe_4OCO_3(OH)_8$, has been obtained.

Ferric Oxide. (Iron Sesquioxide or Peroxide)

Ferric oxyhydroxide, $FeO(OH)$, decomposes when heated to low redness, ferric oxide, Fe_2O_3, remaining.

$$2FeO(OH) = Fe_2O_3 + H_2O$$

Experiment 12.—Roast a crystal or two of ferrous sulphate, mixed with a small quantity of sulphur to aid the reduction, in a small crucible until fumes are no longer evolved; the residue is a variety of ferric oxide, known in trade as *red oxide of iron, colcothar, crocus, mineral rouge, Venetian red,* etc. It has sometimes been used in pharmacy in mistake for the oxyhydroxides, from which it differs not only in composition but in the important respect of being almost insoluble in acids.

Ferric Acetate. Iron Acetate

Experiment 13.—Digest recently-prepared, washed, and drained ferric hydroxide in glacial acetic acid; ferric acetate, $Fe(C_2H_3O_2)_3$, is produced:—

$$\underset{\text{Ferric hydroxide}}{Fe(OH)_3} + \underset{\text{Acetic acid}}{3HC_2H_3O_2} = \underset{\text{Ferric acetate}}{Fe(C_2H_3O_2)_3} + \underset{\text{Water}}{3H_2O}$$

When the ferric hydroxide of this reaction is prepared from $2\frac{1}{2}$ fluid ounces of the official solution of ferric sulphate (p. 171), and is dissolved in $1\frac{1}{2}$ fluid ounces of liquefied glacial acetic acid, the whole being diluted with water to 20 fluid ounces, the product is *Liquor Ferri Acetatis,* B.P.

The "Scale" Compounds of Iron

Experiment 14.—Repeat experiment 11, introducing some solution of citric or tartaric acid or of acid potassium tartrate into the ferric sulphate solution before adding it to the alkali (caustic soda, caustic potash, or ammonia), and notice that now no precipitation of ferric hydroxide occurs. The non-production of precipitates is due to the formation of double compounds, which remain in solution along with alkali-metal sulphate. Such ferric compounds, made by mixing certain prescribed proportions of recently prepared ferric hydroxide (from which all soluble sulphate has been removed by washing), with the respective acids (tartaric or citric) or acid salts (acid potassium tartrate), etc., evaporating the solutions to a syrupy consistence and then spreading on smooth plates to dry, form scale preparations such as *Ferri et Ammonii Citras*, B.P., and *Ferrum Tartaratum*, B.P. A mixture of ferric citrate with ammonium citrate and quinine citrate yields, by similar treatment, the well-known scales of *Ferri et Quininæ Citras*, B.P.

Specimens of these substances may be prepared by attending to the following details. It is essential, first, that the ferric hydroxide be thoroughly washed, or an insoluble oxysulphate will be formed; secondly, that the ferric hydroxide be rapidly washed, or an insoluble ferric oxyhydroxide will be produced; thirdly, that the whole operation be conducted quickly, or reduction to green ferrous salt will occur; fourthly, that the solutions of the salts be not evaporated at a higher temperature than that stated in the official directions, or decomposition will take place; and, fifthly, that excess of ferric hydroxide be employed.

In the pharmacopœial processes for the three scale compounds, the ferric hydroxide is in each case freshly made from solution of ferric sulphate by precipitation with solution of ammonia:—

$$\underset{\substack{\text{Ferric}\\\text{sulphate}}}{Fe_2(SO_4)_3} + \underset{\substack{\text{Ammonia}\\\text{water}}}{6NH_3 + 6H_2O} = \underset{\substack{\text{Ferric}\\\text{hydroxide}}}{2Fe(OH)_3} + \underset{\substack{\text{Ammonium}\\\text{sulphate}}}{3(NH_4)_2SO_4}$$

the solution of ferric sulphate being made of a definite concentration from a known weight of ferrous sulphate. The reason for adopting this course is, that ferric hydroxide cannot be dried without decomposing and becoming insoluble as explained on p. 172, and therefore cannot be weighed. This definite solution of ferric sulphate (*Liquor Ferri Persulphatis*, B.P.) is made as already described.

Ferri et Ammonii Citras, B.P.—Ferric hydroxide is dissolved in solution of citric acid, solution of ammonia added, and the whole evaporated to dryness.

To prepare the ferric hydroxide, dilute 10 fluid ounces of the above solution of ferric sulphate with about a quart of water; pour this into 2 pints of water containing excess of solution of ammonia. (If the opposite course were adopted—the alkaline liquid poured into the ferric solution—the precipitate would contain ferric oxysulphate, or hydroxysulphate, which interferes with the brilliancy of the scales.) Thoroughly stir the mixture (it will smell strongly of ammonia if enough of the latter has been used), allow the precipitate to subside, pour away the supernatant liquid, add more water, and repeat the washing until a white precipitate of barium sulphate is no longer produced on the addition of solution of barium chloride or nitrate to a little of the washings. Collect the ferric hydroxide on a filter, drain, and add it, while still moist, to a solution of 4 ounces of citric acid in 4 of water, placed in an evaporating-basin on a water-bath; stir frequently, until nearly the whole of the hydroxide has dissolved, or until the acid is fully saturated with the hydroxide and some of the latter remains undissolved. To the mixture, when cold, add $5\frac{1}{2}$ fluid ounces of solution of ammonia, filter, evaporate on a water-bath to the consistence of syrup, spread thinly on sheets of glass, and dry (at a temperature not exceeding 100° F., 37·8° C.). The product scales off the glass in deep-red transparent laminæ.

Note.—The chemical composition of iron and ammonium citrate is approximately $FeO(NH_4)_2C_6H_5O_7$. Compounds which exhibit an analogy in composition are found in bismuth and ammonium citrate, $BiO(NH_4)_2C_6H_5O_7$, and antimony and potassium tartrate, $SbOKC_4H_4O_6$.

Ferri et Quininæ Citras, B.P.—Ferric hydroxide and pure quinine are dissolved in solution of citric acid, solution of ammonia added, and the whole evaporated to dryness. The product contains ferric citrate, quinine citrate, and ammonium citrate.

The ferric hydroxide is obtained from 9 fluid ounces of the solution of ferric sulphate, with all the precautions described under *Ferri et Ammonii Citras,* a proportionate quantity of solution of ammonia being employed.

While the ferric hydroxide is being washed, prepare the quinine by dissolving 2 ounces of quinine sulphate in 16 ounces of distilled water, acidulated with sufficient sulphuric acid to dissolve the sulphate (about 3 fluid ounces of the official "diluted sulphuric acid"), and to the clear liquid add solution of ammonia, well mixing the product by stirring, until the whole of the quinine is precipitated (this is the case when the mixture, after thorough agitation, smells of ammonia). Collect the precipitate on a filter, let it drain, and wash away adhering solution of ammonium sulphate by passing through it about three pints of distilled water.

The ferric hydroxide and quinine being now washed and drained, dissolve the former, and afterwards the latter, in a solution of 6 ounces and 60 grains of citric acid in an equal weight of distilled water, the acid liquid being warmed on a water-bath, and portions of the precipitates stirred in as fast as solution is effected. "Let the solution cool; add, in small quantities at a time, 3 fluid ounces of solution of ammonia, diluted with 4 fluid ounces of distilled water; stir briskly, allowing the quinine which separates with each addition of ammonia to dissolve before the next addition is made; filter the solution; evaporate it to the consistence of a thin syrup; dry the latter in thin layers on flat porcelain or glass plates at a temperature of 100° F. (37·8° C.); remove the dry scales of Iron and Quinine Citrate."

Ferri et Strychninæ Citras is included in the United States Pharmacopœia.

Ferrum Tartaratum, B.P. (*Ferri et Potassii Tartras,* U.S.P.) —Ferric hydroxide is dissolved in solution of acid potassium tartrate, and the whole evaporated to dryness.

The ferric hydroxide obtainable from 10 fluid ounces of the official solution of ferric sulphate by the action of ammonia, in the manner detailed under *Ferri et Ammonii Citras,* is mixed (in a porcelain dish), while still moist but well drained, with 3 ounces and 146 grains of acid potassium tartrate. The whole is set aside for about twenty-four hours, and then heated on a water-bath to a temperature not exceeding 140° F.

(60° C.); a pint and a half of distilled water is then added, and the mixture is kept warm until nothing more will dissolve, filtered, evaporated at a temperature not exceeding 140° F. (60° C.) (greater heat causes decomposition), and when the mixture has the consistence of syrup, spread on sheets of glass and allowed to dry (in any warm and open place at a temperature not exceeding 100° F., 37·8° C.). The dry salt is thus obtained in scales. It should be kept in well-closed bottles.

The foregoing are the official (B.P.) scale preparations of iron. Many others of similar character might be formed. Few of them crystallize or give other indications of definite chemical composition. Their properties are only constant so long as they are made with unvarying proportions of the constituents. A crystalline *ferrous tartrate,* $FeC_4H_4O_6$, and an *acid ferrous citrate,* $FeHC_6H_5O_7, H_2O$, have been obtained by the interaction of iron and the respective acids in hot water. They occur as white gritty masses of microscopic crystals. A *sodio-ferrous citrate,* $FeNaC_6H_5O_7$, and *hydroxycitrate,* $FeOHNa_2C_6H_5O_7$, may be obtained in scales. In the United States Pharmacopœia *Ferri Citras* and *Ferri et Ammonii Tartras* are included. The former dissolves slowly in cold, but readily in warm water. *Ferric phosphate,* $FePO_4$, when freshly precipitated, is soluble in solutions of citrates of the alkali-metals, and the solutions on evaporation on glass plates yield scales. *Ferri Pyrophosphas Solubilis* is also included in the U.S.P.

Wine of iron, or "Steel" wine (*Vinum Ferri,* B.P.), made by digesting iron wire in sherry wine, probably contains a little iron and potassium tartrate and other iron salts, formed by action of the metal on the small quantities of acid potassium tartrate and tartaric, citric, malic, and acetic acids present in the wine. *Vinum Ferri Citratis,* B.P., is a solution of iron and ammonium citrate in orange wine.

Ferric Nitrate. (Iron Pernitrate)

Experiment 15.—Place a few iron tacks in dilute nitric acid and set aside; solution of ferric nitrate, $Fe(NO_3)_3$, is formed.

$$\underset{\text{Iron}}{Fe} + \underset{\text{Nitric acid}}{4HNO_3} = \underset{\text{Ferric nitrate}}{Fe(NO_3)_3} + \underset{\text{Water}}{2H_2O} + \underset{\text{Nitric oxide}}{NO}$$

This solution made with care and of a prescribed strength, forms *Liquor Ferri Pernitratis,* B.P. The process is as follows:

—$4\frac{1}{2}$ fluid ounces of nitric acid are diluted with 16 ounces of distilled water, and 1 ounce of iron wire, free from rust, is dissolved in the mixture, the latter being kept cool to moderate the action. The liquid is filtered and diluted to 30 fluid ounces.

Ferric nitrate and ferric acetate unite to form various acetonitrates, amongst which is one having the formula $Fe_2(C_2H_3O_2)_4NO_3OH, 4H_2O$, and crystallizing in hard, shining brownish-red prisms.

Reduced Iron

Experiment 16.—Pass pure hydrogen (which has been dried by passing it over pieces of calcium chloride contained in a tube or through sulphuric acid in a wash-bottle) over a small quantity of ferric oxide, Fe_2O_3, or ferric oxyhydroxide, $FeO(OH)$, contained in a tube placed horizontally, the powder being kept hot by a gas-flame; oxygen is removed by the hydrogen, steam escapes at the open end of the tube, and after a short time, when moisture ceases to be evolved, metallic iron, in a state of fine division, remains. (*See* fig. 32.)

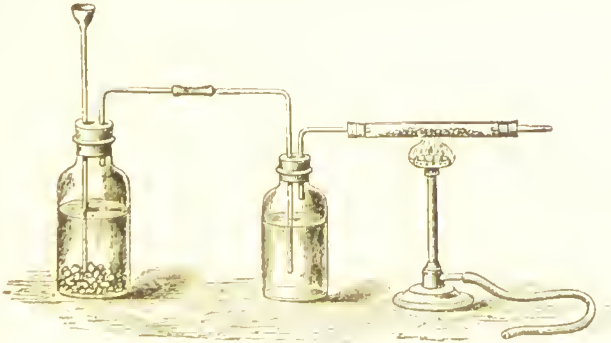

FIG. 32.—Preparation of Reduced Iron.

$$\underset{\text{Ferric oxyhydroxide}}{2FeO(OH)} + \underset{\text{Hydrogen}}{3H_2} = \underset{\text{Iron}}{2Fe} + \underset{\text{Water}}{4H_2O}$$

While still hot, throw the iron out into the air; it takes fire and falls to the ground as magnetic oxide, Fe_3O_4.

If ferric oxide is reduced in a strongly-heated iron tube in a furnace, the particles of iron aggregate to some extent, and, when cold, are only slowly oxidized in dry air. This latter form of reduced iron is *Fer réduit*, or *Quevenne's Iron*, the *Ferri pulvis*, or *Ferrum Redactum*, B.P.—"a fine greyish-black powder, strongly attracted by the magnet, and producing metallic streaks when rubbed with firm pressure in a mortar." It is often administered in the form of a lozenge (*Trochiscus Ferri Redacti*, B.P.), gum and sugar protecting the iron from oxidation as well as forming a vehicle for its administration.

Note 1.—The spontaneous ignition of the iron in the above experiment is an illustration of the influence of minute division on the occurrence of chemical change. The action is the same as that which occurs when iron wire burns (as it does with great brilliancy) in oxygen. The surface exposed to the action of the oxygen of the air is, in the case of this variety of reduced iron, so enormous compared with the weight of the iron, that the heat is not conducted away sufficiently fast to prevent elevation of temperature to a point at which the whole becomes incandescent. The mixture of lead and carbon (lead pyrophorus) resulting when lead tartrate is carefully heated in a test-tube until fumes cease to be evolved, spontaneously ignites when thrown into the air, and for the same reason. Many substances, solid and liquid, if liable to oxidation, and sufficiently finely divided, and especially if exposed in a warm place, become hot and even occasionally burst into flame spontaneously. Oil on cotton waste, powdered charcoal, coal (especially if pyritic, porous, or powdered), resins in powder, and even flour and hay, are familiar illustrations of materials liable to "heat," char, or even burn spontaneously.

Note 2.—The student who has time and opportunity to do so, is advised to carry out experiment 16, as a roughly quantitative one, by way of realizing what has already been stated (see *Laws of Chemical Combination*, pp. 42, 43), with respect to chemical actions, that they take place between definite weights only of matter. Three tubes, similar to the oxide tube shown in fig. 32 (or three U tubes), should be prepared, the second being connected to the first, and the third to the second, in the usual manner, by means of indiarubber tubing. The first tube should contain pieces of calcium chloride to absorb any traces of moisture not retained by the sulphuric acid. The second tube (the ends of the small tube being temporarily closed by small corks) should be weighed in a balance which will turn with a quarter of or half a grain, and, the weight having been noted, 159 grains of dry ferric oxide should be neatly placed in the middle of the tube. (The oxide, before being weighed must be heated in a small crucible over a Bunsen flame to convert any ferric oxyhydroxide into ferric oxide, and to remove all traces of moisture.) The third tube should contain pieces of calcium chloride to absorb the water produced in the reaction, and should be weighed just before being connected. The operation is now carried out. At its close, and when the middle tube is cold, the latter and the third tube are again weighed. The oxide tube should weigh nearly 48 (47·64) grains less than before, and the calcium chloride tube nearly 54 (53·64) grains more than before.

$$\underbrace{Fe_2O_3}_{(111{\cdot}2+47{\cdot}64)} + \underbrace{3H_2}_{6} = \underbrace{2Fe}_{111{\cdot}2} + \underbrace{3H_2O}_{53{\cdot}64}$$

The operation is completed more quickly if one-half or one-fourth of the weight of oxide be taken; in that case one-half or one-fourth of the weights of iron and of water will be obtained. Indeed any weight of oxide may be employed; the amount of iron and water resulting will be *always exactly proportionate* to the weights just mentioned, provided the whole of the ferric oxide is reduced to iron.

Analytical Reactions of Iron Salts.

Reactions of Ferrous Salts.

1. Pass hydrogen sulphide, H_2S, through a solution of a ferrous salt (*e.g.*, ferrous sulphate) slightly acidulated with hydrochloric acid; no precipitate is produced. This is a valuable negative fact, as will be evident presently.

2. Add ammonium hydrosulphide, NH_4SH, to solution of a ferrous salt; a black precipitate of ferrous sulphide, FeS, is produced.

$$FeSO_4 + 2NH_4SH = FeS + (NH_4)_2SO_4 + H_2S$$

3. Add solution of potassium ferrocyanide (yellow prussiate of potash), $K_4FeC_6N_6$, to a solution of a ferrous salt; a

pale blue precipitate is produced, which rapidly becomes darker blue owing to absorption of oxygen and conversion into Prussian blue. (*See* p. 181.)

4. To a solution of a ferrous salt add potassium ferricyanide (red prussiate of potash), $K_3FeC_6N_6$; a dark blue precipitate is produced of Turnbull's blue, resembling Prussian blue.*

Other Analytical Reactions.—The precipitates produced from ferrous solutions on the addition of alkali-metal carbonates, phosphates, and arsenates, as already described in the experiments dealing with the preparation of the corresponding ferrous salts, are characteristic, and hence have a certain amount of analytical interest, but are inferior in this respect to the four reactions above mentioned.

Note.—Solution of ammonia, and solutions of caustic potash and soda in presence of ammonium salts, are incomplete precipitants of ferrous salts. To a solution of a ferrous salt add ammonia; on filtering off the whitish ferrous hydroxide, and testing the filtrate with ammonium hydrosulphide, iron will still be found in solution. To another portion of the ferrous solution add a few drops of nitric acid, or excess of chlorine water, and boil; this converts the ferrous into ferric salt, and alkalies, including ammonia, will now precipitate the iron completely as ferric hydroxide.

In actual analysis, the separation of iron as ferric hydroxide is an operation of frequent performance. This is always accomplished by the addition of alkali after (if the iron occurs as a ferrous salt) previous ebullition with a little nitric acid. Potassium ferrocyanide and ferricyanide are the reagents most commonly used in distinguishing ferrous from ferric salts.

Reactions of Ferric Salts.

1. Through a solution of a ferric salt (*e.g.*, ferric chloride) pass hydrogen sulphide; a white precipitate of sulphur (from the hydrogen sulphide), is produced. The ferric

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* Cyanogen (CN′, or Cy′), ferrocyanogen (FeC_6N_6'''', or $FeCy_6''''$) and ferricyanogen (FeC_6N_6''', or $FeCy_6'''$) are radicals which play the part of non-metallic elements, just as ammonium in its chemical relations resembles the metallic elements. They will be referred to again.

salt is simultaneously converted into a ferrous salt, the latter remaining in solution. This reaction is of frequent occurrence in analysis:—$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S$.

2. Add ammonium hydrosulphide to a solution of a ferric salt; the latter is reduced to the ferrous state, and a black substance (ferrous sulphide, FeS) is precipitated, as in the second analytical reaction of ferrous salts, sulphur being set free.

3. To a solution of a ferric salt add potassium ferrocyanide, $K_4FeC_6N_6$; a precipitate of Prussian blue (the well-known pigment), is produced.

4. To a solution of a ferric salt add potassium ferricyanide; no precipitate is produced, but the liquid assumes a dark brownish red colour (or a greenish or olive hue if the salts are not quite pure).

5. Add caustic potash, caustic soda, or ammonia to a solution of a ferric salt; a reddish-brown precipitate of ferric hydroxide, $Fe(OH)_3$, is produced (compare experiment 11, p. 171).

Other Analytical Reactions.—Some of these have occasional interest. In neutral ferric solutions the tannic acid in aqueous infusion of galls occasions a bluish-black inky precipitate, the basis of most black writing-inks.—Potassium thiocyanate, KSCN, causes the formation of ferric thiocyanate, which is of a deep blood-red colour. The colour disappears on the addition of mercuric chloride.

There is no normal ferric carbonate; alkali-metal carbonates cause the precipitation of ferric hydroxycarbonate whilst carbonic anhydride escapes.

QUESTIONS AND EXERCISES

Name the chief ores of iron.—How is the metal obtained from the ores?—What is the chemical difference between cast-iron, wrought-iron, and steel? Explain the process of "welding."—What is the nature of chalybeate waters?—Illustrate by formulæ the difference between ferrous and ferric salts.—Write a paragraph on the nomenclature of iron salts.—Give a diagram of the process for the preparation of ferrous sulphate.—In what respects do the official Ferrous Sulphate and Exsiccated Ferrous Sulphate differ?—How is ferrous sulphate obtained on the large scale?—Give the chemical names of white, green, and blue vitriols.—Why does ferrous sulphate become brown on exposure to air?—Represent by an equation the formation of Ferrous Carbonate.—Describe the action of atmospheric oxygen on ferrous carbonate; can the effect be prevented?—In what order would you mix the ingredients of *Mistura Ferri Composita*, and why?—Write out an equation illustrative of the formation of the official Iron Phosphate.—Why is sodium bicarbonate used in the preparation of ferrous phosphate?—Name four iron compounds which may be formed by the direct union of their elements.—Give the official method for the preparation of Solution of Ferric Chloride. —How may Ferrous be converted into Ferric Sulphate?—What is the formula of Ferric Acetate, and how is it prepared for use in pharmacy?—How does Ferric Hydroxide act as an antidote in arsenical poisoning?—What are the properties of ferric oxide?—What are the general characters and mode of production of the medicinal scale preparations of iron?—In what state is the iron in *Vinum Ferri*, B.P.?—What other form of Iron Wine is official?—Give a diagram showing the formation of Ferric Nitrate.—Calculate how much ferric oxide will yield, theoretically, one hundredweight of iron. *Ans.*, 160 lbs., approximately.—Describe the action of each of the following reagents on solutions of iron salts, distinguishing between ferrous and ferric reactions, and illustrating each of the reactions by an equation:—*a.* Ammonium hydrosulphide. *b.* Potassium ferrocyanide. *c.* Potassium ferricyanide. *d.* Caustic Alkalies. *e.* Potassium thiocyanate.—Describe the action of ammonia on salts of iron, aluminium, and zinc respectively.

CHROMIUM: Cr. Atomic weight, 51·74

Occurrence.—The chief ore of chromium is chrome ironstone, FeO,Cr_2O_3, *chromite*, occurring chiefly in the United States and in Sweden. The metal may be isolated by the action of aluminium on chromic oxide, Cr_2O_3, at a very high temperature.

Chromium forms sets of salts corresponding to chromous and chromic oxides, CrO and Cr_2O_3 respectively, but the chromous salts are exceedingly readily converted by processes of oxidation into chromic salts, and can only be prepared and preserved with difficulty. The ordinary salts in which chromium plays the part of the metallic radical, are the chromic salts, such as chromic chloride, $CrCl_3$; chromic sulphate, $Cr_2(SO_4)_3$; etc. Chromium also forms an acid anhydride, *chromic anhydride*, CrO_3, and the best known chromium compounds—the chromates (*e.g.*, potassium chromate, K_2CrO_4), and the bichromates or anhydrochromates (*e.g.*, potassium bichromate, K_2CrO_4,CrO_3 or $K_2Cr_2O_7$) in which the chromium forms a part of the complex acid radicals CrO_4'' and Cr_2O_7''—are referred to the unknown chromic acid [H_2CrO_4] and anhydrochromic acid [$H_2Cr_2O_7$], corresponding to this anhydride. Most of the commoner chromium compounds are obtained from potassium bichromate.

Preparation of Potassium Bichromate.—On roasting powdered chrome iron ore with potassium carbonate and nitrate, yellow potassium chromate, K_2CrO_4, is obtained; the mass, treated with acid, yields red potassium bichromate, K_2CrO_4,CrO_3, or $K_2Cr_2O_7$ (*Potassii Bichromas*, B.P.):—

$$2K_2CrO_4 + 2HCl = K_2Cr_2O_7 + 2KCl + H_2O$$

From this, other chromates are prepared, and, by reduction, as presently explained, the chromic salts.

Heated strongly in a crucible, potassium bichromate splits up into potassium chromate, glistening green chromic oxide, and oxygen, $4K_2Cr_2O_7 = 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$. Ammonium bichromate, when heated yields several times its volume of bluish-green chromic oxide, water, and nitrogen. $(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2$. The yellow and orange lead chromates (lead chromate, $PbCrO_4$, and basic lead chromate, Pb_2OCrO_4), are used as pigments.

Potassium Chromate.—The normal or yellow potassium chromate is obtained on adding potassium bicarbonate, 200 grains, in small quantities at a time, to a hot solution of the bichromate, about 295 grains, until effervescence ceases.

$$K_2Cr_2O_7 + 2KHCO_3 = 2K_2CrO_4 + 2CO_2 + H_2O$$

For analytical purposes solution of a *normal chromate* is still more readily prepared by simply adding solution of ammonia to a solution of potassium bichromate, until the liquid turns yellow and, after stirring, smells of ammonia.

$$K_2Cr_2O_7 + 2NH_4OH = K_2CrO_4 + (NH_4)_2CrO_4 + H_2O$$

Conversion of a chromate (in which chromium forms part of an acid radical) into chromic salt (in which chromium is the metallic radical).—Through an acidulated solution of potassium bichromate pass hydrogen sulphide: sulphur is deposited, and a green chromic salt remains in solution—chromic chloride, $CrCl_3$, if hydrochloric acid be used, and sulphate, $Cr_2(SO_4)_3$, if sulphuric be the acid employed. Boil the liquid to expel excess of hydrogen sulphide, filter, and reserve the solution for subsequent experiments. (For an equation representing this reaction, *see* p. 185.) Alcohol, sugar, and various other substances which are moderately easily oxidized answer as well as hydrogen sulphide. For a method of carrying out the reverse operation to that just described, *i.e.*, the conversion of a chromic salt into a chromate, see the dry-way reaction for chromium compounds in general on p. 186.

Chromic sulphate, $Cr_2(SO_4)_3$, like aluminium sulphate, $Al_2(SO_4)_3$, unites with alkali-metal sulphates to form double salts which are called *alums*. These alums resemble common alum in crystalline form; but they do not contain aluminium, the place of the latter being taken by chromium: they are of a purple colour.

Chromic Anhydride

Experiment.—Mix four volumes of a cold saturated aqueous solution of potassium bichromate with five of sulphuric acid; on cooling, *chromic anhydride*, often called *chromic acid*, CrO_3, (*Acidum Chromicum*, B.P.) separates in crimson needles. After well draining, the crystals may be freed from adhering sulphuric acid by washing once or twice with nitric acid: the latter may be removed by passing dried and slightly warmed air through a tube containing the crystals. Chromic anhydride may also be freed from sulphuric acid by one or two recrystallizations. In contact with moisture, chromic anhydride takes up water and forms a solution of anhydrochromic acid [$H_2Cr_2O_7$], 1 part of the anhydride and 3 of water forming the *Liquor Acidi Chromici*, B.P. Chromic anhydride is a powerfully corrosive oxidizing agent; it melts between 356° and 374° F. (180° to 190° C.), and at a higher temperature decomposes, yielding chromic oxide and oxygen; it oxidizes organic matter with great violence, spontaneous ignition sometimes resulting.

In the systematic analytical examination of solutions containing chromates, the chromium is precipitated as green hromic hydroxide along with ferric and aluminium ydroxides, the prior treatment with hydrogen sulphide in resence of hydrochloric acid reducing the chromate to the ondition of a chromic salt, thus :—

$$2K_2Cr_2O_7 + 16HCl + 6H_2S = 4CrCl_3 + 4KCl + 14H_2O + 3S_2$$

hromium having been found in a solution, its condition as hromate may be ascertained by noting the yellow or orange olour of the solution ; by observing the precipitation of sulhur, as above, with simultaneous change in colour from orange o green when the acidulated solution is treated with excess f hydrogen sulphide ; and by applying to the solution, salts f barium, mercury, lead, and silver. (*See* the various pararaphs relating to those metals.)

$Ba(NO_3)_2$	gives	yellow	$BaCrO_4$	with chromates.
$HgNO_3$	,,	red	Hg_2CrO_4	,,
$AgNO_3$	,,	red	Ag_2CrO_4	,,
$AgNO_3$	,,	red	$Ag_2Cr_2O_7$	with bichromates.
$Pb(C_2H_3O_2)_2$	,,	yellow	$PbCrO_4$	with both.

Barium nitrate does not completely precipitate bichromtes, barium bichromate being soluble in water ; barium romate is insoluble in water and in acetic acid, but soluble hydrochloric or nitric acid. Mercurous nitrate does not holly precipitate bichromates : mercuric nitrate or chloride ly partially precipitates chromates, and does not precipite bichromates. Mercurous chromate is insoluble, or nearly , in dilute nitric acid. Silver chromate and bichromate are luble in acids and alkalies. Lead acetate precipitates lead hromate from both chromates and bichromates, acetic acid beng set free in the latter case ($K_2Cr_2O_7 + 2Pb(C_2H_3O_2)_2 + H_2O$ $2PbCrO_4 + 2KC_2H_3O_2 + 2HC_2H_3O_2$).

A delicate reaction for dry chromates depends on the rmation of *chromyl chloride* or *chlorochromic anhydride*, CrO_2Cl_2. small portion of the chromate is placed in a test-tube with fragment of dry sodium chloride and a drop or two of suluric acid, and the mixture is heated ; red irritating fumes chlorochromic anhydride are evolved, and condense in dark d drops on the side of the tube.

Larger quantities are obtained by the same reaction, the operation being conducted in a retort, with thoroughly dry materials, as the compound is decomposed by water. Chlorochromic anhydride may be regarded as chromic anhydride in which an atom of oxygen is displaced by an equivalent quantity (two atoms) of chlorine. It is not used in medicine, but is of interest to the student as an example of a class of compounds known as *acichlorides.* The reaction is also occasionally serviceable for the detection of chlorides. (*See* p. 297.)

Analytical Reactions of Chromic Salts.

1. To a solution of a chromic salt (chloride, sulphate, or chrome alum) add ammonium hydrosulphide; a bulky green precipitate of chromic hydroxide, $Cr(OH)_3$, is produced.

$$CrCl_3 + 3NH_4SH + 3H_2O = Cr(OH)_3 + 3NH_4Cl + 3H_2S$$

2. To a solution of a chromic salt, add ammonia; green chromic hydroxide is precipitated, insoluble in excess.

3. To a solution of a chromic salt add solution of caustic potash or caustic soda drop by drop; green chromic hydroxide is precipitated. Add excess of the alkali; the precipitate is dissolved. Boil the solution for some time; chromic hydroxide is reprecipitated.

Chromic Oxyhydroxides. — Intermediate in composition between chromic hydroxide, $Cr(OH)_3$, and chromic oxide, Cr_2O_3, two oxyhydroxides are known, namely, $Cr_2O(OH)_4$ and $CrOOH$.

Dry-way Reaction for Chromium Compounds in general.—Mix a small quantity of any chromium compound with sodium carbonate and a few grains of nitre on platinum foil, and fuse the mixture in the blowpipe-flame; a yellow mass (potassium and sodium chromates) is formed. Dissolve the mass in water, add acetic acid to decompose excess of carbonate, and apply the reagents for chromates. This is a delicate and useful reaction if carefully performed.

The production of the chromate from a chromic salt in the above reaction may be represented by the equation:—
$2CrCl_3 + 5Na_2CO_3 + 3O = 2Na_2CrO_4 + 6NaCl + 5CO_2$.

DIRECTIONS FOR APPLYING THE ANALYTICAL REACTIONS DESCRIBED IN THE FOREGOING PARAGRAPHS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS CONTAINING ONE OF THE METALS, ALUMINIUM, IRON, CHROMIUM.*

First note the colour of the solution :—

Solutions of aluminium salts are colourless.
Solutions of ferrous salts are colourless or pale green.
Solutions of ferric salts are yellow or brownish.
Solutions of chromic salts are bluish-purple or green.

Add solution of ammonia (the group-reagent) gradually :—

A white precipitate, insoluble or nearly so in excess, indicates an aluminium salt.

A dirty-green precipitate indicates iron in the state of a ferrous salt.

A reddish-brown precipitate indicates iron in the state of a ferric salt.

A bluish-grey precipitate, insoluble or nearly so in excess, indicates a chromic salt.

These results may be confirmed by the application of some of the other tests to fresh portions of the solution.

ABLE OF SHORT DIRECTIONS FOR APPLYING THE ANALYTICAL REACTIONS DESCRIBED IN THE FOREGOING PARAGRAPHS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ONE, TWO, OR ALL THREE OF THE METALS, ALUMINIUM, IRON, CHROMIUM.

Boil about one-third of a test-tubeful of the solution with a few drops of nitric acid. This ensures the conversion of ferrous into ferric salt, and enables the next reagent (ammonia) *completely* to precipitate the iron. Add a slight excess of ammonia and shake the mixture; filter. Wash the precipitate, dry it, and fuse it on platinum foil with sodium carbonate and potassium nitrate. Boil the fused mass in water, and filter.

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* The analytical behaviour of chromium in the chromic salts is alone referred to here. In the systematic examination of solutions for other metallic radicals besides those hitherto considered, any chromate or bichromate originally present is converted into chromic salt before the stage is reached at which aluminium, iron, and chromium are tested for. (Note, however, that solutions of chromates and bichromates are yellow and orange respectively.)

Residue	*Filtrate*	
Fe_2O_3 brown. (*Note* 1)	If yellow, Cr is present and has formed chromate during the fusion. Divide into two parts.	
	1 Add NH_4Cl and warm. White ppt. indicates Al.	2 Add acetic acid in excess and $AgNO_3$. Red ppt. indicates Cr.

Note 1.—If iron is present, portions of the original solution must be tested with potassium ferricyanide for ferrous, and with potassium ferrocyanide for ferric salts; dark-blue precipitates with both indicate both ferrous and ferric salts.

Note 2.—If ferrous salt is not present, the preliminary ebullition with nitric acid is unnecessary. It is perhaps therefore advisable always to determine this point *previously* by testing a little of the original solution with potassium ferricyanide; if no blue precipitate is produced, the nitric-acid treatment may be omitted.

Cerium: Ce. At. wt., 139·2.—This element occurs in the mineral cerite (which contains iron, calcium, and the rare metals, cerium, lanthanum, and didymium [the latter really a mixture of neodymium and praseodymium] as silicates); also occasionally as impure fluoride, carbonate, and phosphate. The oxalate, *Cerii Oxalas*, B.P., a white granular powder, is the only official salt; it may be obtained from cerite by boiling the powdered mineral in concentrated hydrochloric acid for several hours, evaporating, diluting, and filtering to separate silica; adding solution of ammonia to precipitate hydroxides of all the metals except calcium; filtering, washing, redissolving in hydrochloric acid, and adding oxalic acid to precipitate cerium oxalate. The preparation still contains lanthanum and didymium oxalates; it is therefore strongly calcined, the resulting lanthanum and didymium oxides dissolved out to some extent by boiling with a concentrated solution of ammonium chloride, the residual rium oxide dissolved in boiling hydrochloric acid, and am-onium oxalate added to precipitate cerium oxalate, $Ce_2(C_2O_4)_3$, H_2O. According to Hartley, the precipitated hydroxides ould be treated with chlorine, by which ceric hydroxide is ft insoluble and the other hydroxides converted into soluble ypochlorites.

The oxalate is insoluble in water. It is decomposed at a ll-red heat, 47 per cent. of a yellow or, generally, salmon-loured mixture of oxides remaining. Usually the didymium resent gives the ignited residue a reddish or reddish-brown lour. The oxides are soluble in boiling hydrochloric acid vithout effervescence, indicating, indirectly, absence of rthy and other carbonates or oxalates); and the solution ives, with excess of a saturated solution of potassium sul-hate, a crystalline precipitate of double cerium and potas-um sulphate. Alumina mixed with cerium oxalate may be etected by boiling with solution of potassium hydroxide, tering, and adding excess of solution of ammonium chloride, hen a white flocculent precipitate (aluminium hydroxide) ill be obtained. The oxalic radical is recognised by neutral-ing the potassium hydroxide solution with acetic acid, and lding calcium chloride; a white precipitate (calcium oxalate) lls: this precipitate, though insoluble in acetic acid, should wholly soluble in hydrochloric acid. Acid or neutral rium solutions give with sodium acetate and hydrogen per-xide a brownish-red colour (Hartley).

QUESTIONS AND EXERCISES

State the method of preparation of potassium bichromate.—Give e formulæ of potassium chromate and bichromate.—How is potas-um chromate obtained?—Describe the action of hydrogen sulphide n acidulated solutions of chromates.—What is the formula of chrome um?—Mention the chief tests for chromates and for chromic salts.—hat are the formula and properties of cerium oxalate?

ARSENIUM and ANTIMONY

These elements, especially antimony, resemble metals in ppearance and in the character of some of their compounds; ut they are still more closely allied to the non-metals phosphorus and nitrogen, with which they form a natural group. The hydrogen compounds of the four members of this group are represented by the formulæ NH_3, PH_3, AsH_3, SbH_3. A few preparations of arsenium and antimony are used in medicine; but all are more or less powerful poisons, and hence have considerable toxicological interest.

From observations of the vapour density of arsenium, it would appear that the molecule of arsenium contains four atoms, and that its formula is As_4. At temperatures above 1700° C. the vapour density corresponds to the formula As_2.

From observed analogy between the two elements, the molecular constitution of antimony is probably similar to that of arsenium. Vapour density determinations, moreover, lead to the formulæ As_4O_6 and Sb_4O_6 (not As_2O_3 and Sb_2O_3) for arsenious and antimonious oxides.

ARSENIUM: As. Atomic weight, 74·5

Occurrence, etc.—Arsenical ores are frequently met with in nature, the commonest being iron arsenio-sulphide, FeAsS. This "mispickel" is roasted in a current of air, the oxygen of which, combining with the arsenium, forms common *white arsenic* ("arsenic") or arsenious oxide, sometimes called *anhydrous arsenious acid*, or better, *arsenious anhydride*, As_4O_6, (*Acidum Arseniosum*, B.P.), which is condensed in chambers or long flues. It commonly "occurs as a heavy white powder, or in masses which usually present a stratified appearance caused by the presence, in separate layers, of the crystalline and opaque and of the amorphous and vitreous allotropic modifications of arsenious anhydride." The vitreous or amorphous oxide is far more soluble than the crystalline variety, and the two kinds exhibit other differences in properties. Such differences between the crystalline and amorphous varieties of an element or compound or between two crystalline varieties are not infrequent. *Realgar* (red algar) is native red arsenium sulphide, As_2S_2, and orpiment (*auripigmentum*, the golden pigment), is native yellow sulphide, As_2S_3. Arsenious iodide, AsI_3, (*Arsenii Iodidum*, B.P.) may be made from its elements or by dissolving white arsenic in aqueous hydriodic acid and evaporating the solution. It occurs in "small orange-coloured crystals, or crystalline masses, soluble in water and in alcohol (90 per cent.). Its aqueous solution ffords the reactions characteristic of arsenium and of iodides, nd should not change the colour of solution of litmus. Heated n a test-tube, it almost entirely volatilizes, violet vapours of odine being set free." Ebullition with much water gives rise o the formation of a basic salt. A solution of 1 part by weight f arsenious iodide and 1 part by weight of mercuric iodide n 100 fluid parts of water, forms *Liquor Arsenii et Hydrargyri odidi.* B.P. (*Donovan's Solution*).

Alkaline Solution of Arsenic

Experiment 1.—Boil a grain or two of powdered white rsenic, As_4O_6, in a solution of potassium carbonate and filter necessary. The solution, coloured with compound tincture f lavender, and containing 1 part by weight of As_4O_6 in 100 uid parts, forms *Liquor Arsenicalis,* B.P. (*Fowler's Solution*).

Note.—This official solution does not generally contain uch potassium arsenite; for the white arsenic does not ecompose the potassium carbonate, or only after long boiling. From concentrated solutions carbonic anhydride is more uickly eliminated.

Arsenious Acid and other Arsenites

White arsenic, or *arsenious anhydride,* As_4O_6 (formerly called rsenious acid), when dissolved in water yields a solution which ontains some arsenious acid, H_3AsO_3, hydrogen arsenite, and ossesses a faintly acid reaction.

$$\underset{\text{Arsenious anhydride}}{As_4O_6} \quad + \quad \underset{\text{Water}}{6H_2O} \quad = \quad \underset{\text{Arsenious acid}}{4H_3AsO_3}$$

When arsenious anhydride is dissolved in solutions of ustic potash or caustic soda, the anhydride being used in excess, the so-called acid arsenites, $KH(AsO_2)_2$ and $NaH(AsO_2)_2$, re formed. Boiled for some time with excess of the respecve alkali-metal carbonates, these salts yield other arsenites eally metarsenites, as the acid salts also are) the composition f which is represented by the formulæ $KAsO_2$ and $NaAsO_2$.

Arsenious anhydride fused with alkali-metal carbonates ields pyroarsenates ($Na_4As_2O_7$ or $K_4As_2O_7$, as the case may e) and metallic arsenium.

Acid Solution of Arsenic

Experiment 2.—Boil arsenious anhydride with dilute hydrochloric acid; the anhydride slowly dissolves. Such a solution made with prescribed proportions of acid and water, and containing 1 part by weight of As_4O_6 in 100 fluid parts, forms *Liquor Arsenici Hydrochloricus,* B.P. (*De Valangin's Solution* contains a grain and a half per ounce.)

Note.—The student should also boil arsenious anhydride in water only, and thus have an acid, an alkaline, and an aqueous arsenious solution for analytical comparison.

Arsenium

Experiment 3.—Place a grain or less of arsenious anhydride at the bottom of a narrow test-tube, cover it with half an inch or so of small fragments of dry charcoal, and hold the tube, nearly horizontally, in a Bunsen flame, the mouth of the tube being loosely covered by the thumb. At first let the bottom of the tube project slightly beyond the flame, so that the charcoal may become nearly red-hot; then heat the bottom of the tube. The oxide will volatilize, become deoxidized by the hot charcoal, carbonic anhydride being formed, and the element *arsenium* (formerly sometimes termed *arsenicum,* and also sometimes called *arsenic*) will be deposited in the cooler part of the tube as a dark mirror-like metallic coating. During the operation a characteristic odour, resembling garlic, is emitted.

Metallic arsenium may be obtained in large quantities by the above process if the operation be conducted in vessels of appropriate size. Performed on the small scale with great care, in narrow tubes, and using not charcoal alone, but *black flux* (a mixture of charcoal and potassium carbonate obtained by heating acid potassium tartrate in a test-tube or other closed vessel till no more fumes are evolved), the reaction has considerable analytical interest, the garlic odour and the formation of the mirror-like ring being highly characteristic of arsenium. Compounds of mercury and antimony, however, give sublimates which resemble arsenium in appearance and must not be mistaken for it.

Arsenic Acid and other Arsenates

Experiment 4.—Boil a grain or two of arsenious anhydride with a few drops of nitric acid until red fumes are no longer evolved; evaporate the solution to dryness in a small dish, to remove excess of nitric acid; dissolve the residue in water: the product is Arsenic Acid, H_3AsO_4.

Arsenic acid, when strongly heated, loses the elements of water, and arsenic anhydride, As_2O_5, remains. At a still higher temperature arsenic anhydride decomposes, yielding arsenious anhydride and oxygen.

Arsenic anhydride readily absorbs water and becomes arsenic acid, H_3AsO_4. Arsenic acid is reduced to arsenious acid by the action of sulphurous acid. $H_3AsO_4 + H_2SO_3 = H_3AsO_3 + H_2SO_4$.

Salts derived from arsenic acid are termed *arsenates*. The di-ammonium arsenate, $(NH_4)_2HAsO_4$, may be made by neutralizing arsenic acid with ammonia. Its solution in water is occasionally used as a reagent in analysis. Arsenic acid is used as an oxidizing agent in the manufacture of the well-known dye, magenta.

Sodium arsenite and arsenate are used in the cleansing operations of the calico-printer.

Sodium Arsenate and Pyroarsenate

Experiment 5.—Fuse 2 or 3 grains of arsenious anhydride, As_4O_6, with sodium nitrate, $NaNO_3$, and dried sodium carbonate, Na_2CO_3, in a porcelain crucible, and dissolve the resulting mass of sodium pyroarsenate in water; solution of sodium arsenate, Na_2HAsO_4, results.

$$\underset{\substack{\text{Arsenious}\\\text{anhydride}}}{As_4O_6} + \underset{\substack{\text{Sodium}\\\text{nitrate}}}{4NaNO_3} + \underset{\substack{\text{Sodium}\\\text{carbonate}}}{2Na_2CO_3} = \underset{\substack{\text{Sodium}\\\text{pyroarsenate}}}{2Na_4As_2O_7} + \underset{\substack{\text{Nitrous}\\\text{anhydride}}}{2N_2O_3} + \underset{\substack{\text{Carbonic}\\\text{anhydride}}}{2CO_2}$$

$$\underset{\text{Sodium pyroarsenate}}{Na_4As_2O_7} + \underset{\text{Water}}{H_2O} = \underset{\text{Sodium arsenate}}{2Na_2HAsO_4}$$

Crystallized from the solution and dried, a salt is obtained which is represented by the formula $Na_2HAsO_4, 7H_2O$.

The anhydrous salt, Na_2HAsO_4, "obtained by exposing to a temperature of 300° F. (148·9° C.) crystallized sodium arsenate," is official (*Sodii Arsenas*, B.P.). A 1 per cent. aqueous solution forms *Liquor Sodii Arsenatis*, B.P. It has about half the arsenical strength of *Liquor Arsenicalis*, B.P. The anhydrous salt is used because the crystallized salt is of somewhat uncertain composition. The fresh crystals are represented by the formula $Na_2HAsO_4, 12H_2O$ (= 53·7 per cent. of water); these soon effloresce and yield a stable salt having the formula $Na_2HAsO_4, 7H_2O$ (= 40·4 per cent. of water). To avoid the possible employment of a mixture of these salts, the anhydrous salt, of uniform composition, is alone official.

The student will find useful practice in verifying, by calculation, the above numbers representing the centesimal proportion of water in the two sodium arsenates.

The crystalline form of each variety of sodium arsenate ($Na_2HAsO_4, 12H_2O$, and $Na_2HAsO_4, 7H_2O$) is identical with that of the corresponding sodium phosphate ($Na_2HPO_4, 12H_2O$, and $Na_2HPO_4, 7H_2O$), the pairs of analogous composition being isomorphous. This is only one instance of the strong analogy of arsenium and its compounds with phosphorus and its corresponding compounds. The preparation and characters of the next substance, ferrous arsenate, will remind the student of ferrous phosphate.

Ferrous Arsenate. Iron Arsenate

Experiment 6.—To a hot solution of sodium arsenate add a hot solution of ferrous sulphate and a small quantity of a solution of sodium bicarbonate; a precipitate of ferrous arsenate, $Fe_3(AsO_4)_2$, is produced. On a larger scale, $26\frac{1}{2}$ parts of dried sodium arsenate dissolved in 100 of hot water, and $20\frac{3}{4}$ of ferrous sulphate in 120 of hot water, with $4\frac{1}{2}$ of sodium bicarbonate, may be employed. The precipitate should be collected on a calico filter, washed, squeezed, and dried on a water-bath, at a low temperature (100° F., 37·8° C.) to avoid excessive oxidation. It constitutes *Ferri Arsenas*, B.P., “ferrous arsenate, $Fe_3(AsO_4)_2$, $6H_2O$, with ferric arsenate and some iron oxide.”

$$\underset{\text{Sodium arsenate}}{2Na_2HAsO_4} + \underset{\text{Sodium bicarbonate}}{2NaHCO_3} + \underset{\text{Ferrous sulphate}}{3FeSO_4} =$$

$$\underset{\text{Ferrous arsenate}}{Fe_3(AsO_4)_2} + \underset{\text{Sodium sulphate}}{3Na_2SO_4} + \underset{\text{Water}}{2H_2O} + \underset{\text{Carbonic anhydride}}{2CO_2}$$

The use of the sodium bicarbonate is to ensure the absence of free sulphuric acid from the solution. This acid dissolves ferrous arsenate, and it is impossible to prevent its liberation if only the ferrous sulphate and sodium arsenate be employed without the sodium bicarbonate.

At the instant of precipitation ferrous arsenate is white, but it rapidly becomes of a green or greenish-blue colour owing to absorption of oxygen and formation of a ferroso-ferric arsenate. When dry, it is a tasteless, amorphous powder which is soluble in acids and has undergone oxidation to a considerable extent.

Arsenium Hydride and *Sulphides*, and *Copper* and *Silver Arsenites* and *Arsenates* are mentioned in the following analytical paragraphs.

Analytical Reactions of Arsenium Compounds.

1. Repeat experiment 3, operating on not very much more arsenious anhydride than the size of a small pin's head, and using not charcoal alone, but the *black flux* already mentioned, or a well-made and perfectly dry mixture of charcoal and potassium carbonate (the latter salt best obtained by heating potassium bicarbonate). The tube employed should be a narrow test-tube, or better, a tube (easily made from glass-tubing) having the form (Berzelius's) shown in fig. 33.

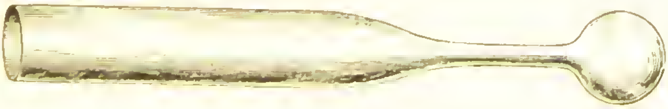

FIG. 33.

The oxide and black flux are placed in the bulb of the tube, which is then heated in a Bunsen flame; the arsenium condenses on the constricted portion of the tube. If now the bulb be carefully removed by fusing and drawing out the glass, the arsenium may be chased up and down the narrower part of the tube until the air in the tube has re-oxidized it to arsenious anhydride.

If the operation has been performed in a less delicate manner in an ordinary test-tube, cut or break off portions of the tube containing the sublimate of arsenium, put them into a test-tube and heat the bottom of the latter, holding it nearly horizontally, and partially closing the mouth of the tube with the finger or thumb; the arsenium combines with oxygen from the air in the tube, and the resulting arsenious anhydride is deposited on the cool part of the tube in brilliant, generally imperfect, octahedral crystals.

Microscopic Examination.—Prove that the crystals are identical in form with those of arsenious anhydride, by heating a grain or less of the latter in another test-tube and examining the two sublimates by means of a good lens or a compound microscope.

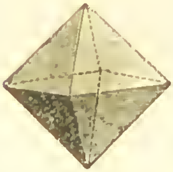

FIG. 34.—Octahedron.

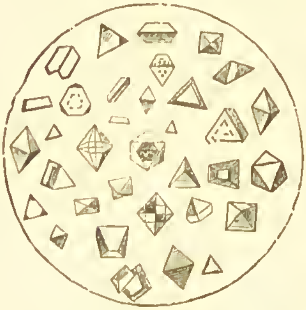

FIG. 34*a*.—A Sublimate of Arsenious Anhydride (Magnified).

The appearance of a sublimate of arsenious anhydride is peculiar and quite characteristic. The primary form of each crystal is an octahedron (ὀκτὼ, *okto*, eight; ἕδρα, *hedra*, side) (fig. 34*a*), or, rarely, a tetrahedron, and in a sublimate a few perfect octahedra are generally present. Usually, however, the crystals are modifications of octahedra such as are shown in fig. 34—which is drawn from actual sublimates.

2. *Reinsch's Test.*—Place a piece of copper foil, about $\frac{1}{4}$

inch wide and ½ inch long, in a solution containing arsenic and hydrochloric acid, and boil (nitric acid must not be present, or the piece of metal will be dissolved); arsenium is deposited on the copper as a grey coating possessing a somewhat metallic appearance. (*Memorandum.*—An equivalent proportion of copper goes into solution. The experiment forms an illustration of a kind of chemical change appropriately termed *substitution.*) Pour off the supernatant liquid from the copper, wash the latter with water, dry it by means of a piece of filter-paper, and finally place it at the bottom of a clean, dry, narrow test-tube, or a Berzelius tube, and sublime as described in reaction 1, again noticing the form of the resulting crystals. The tube containing the sublimate may be reserved for subsequent comparison with a similarly obtained sublimate of antimonious oxide. This test for arsenium was introduced by Reinsch, in 1843.

Note.—Copper itself frequently contains arsenium, a fact that may not, perhaps, cause any trouble to the student, who is performing experiments in practical chemistry with known substances, for educational purposes; but when the analyst proceeds to the examination of substances of unknown composition, he must assure himself that neither his apparatus nor materials already contain the element for which he is searching.

The detection of arsenium in metallic copper is best accomplished by boiling, in a retort or distilling-flask, a mixture of a few grains of the sample with five or six times its weight of ferric hydroxide or chloride (free from arsenium) and excess of hydrochloric acid. The arsenium is thus volatilized in the form of chloride, and may be condensed in water and detected by means of hydrogen sulphide (*see* reaction 6, p. 201) or by Reinsch's test. The ferric chloride solution is, if necessary, freed from any trace of arsenium by evaporating once or twice to dryness with excess of hydrochloric acid.

3. *The Hydrogen Test* or *Marsh's Test.*—Generate hydrogen in the usual way by the interaction of zinc and dilute sulphuric acid, a bottle of about four or six ounces capacity being used, and a funnel-tube and short delivery-tube passing

through the cork as shown in fig. 35. Dry the escaping hydrogen (except in rough experiments, when this is scarcely necessary) by adapting to the delivery-tube a short piece of wider tubing filled with fragments of dried calcium chloride (*a*). To the other end of the drying-tube fit a piece of narrow tubing ten or twelve inches long, made of hard glass, and having its outlet end reduced to a small bore by drawing it out in the flame of the blowpipe. When the hydrogen has been escaping for a sufficient number of minutes and at such a rate as to warrant the student in concluding that *all the air originally present in the bottle has been expelled,* kindle the jet,

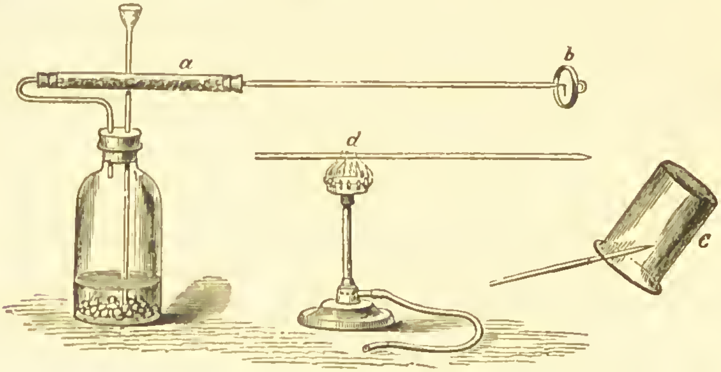

FIG. 35.—The Hydrogen Test for Arsenium.

and then pour eight or ten drops of the aqueous arsenical solution, or three or four drops of the acid or alkaline solution previously prepared, into the funnel-tube, washing the liquid into the generating-bottle by means of a little water. By the action of the zinc and sulphuric acid, the arsenious compound is reduced to the state of arsenium, and the latter combines with some of the hydrogen to form arsenium hydride, arseniuretted hydrogen, or hydrogen arsenide, AsH_3.

$$\underset{\text{Arsenious anhydride}}{As_4O_6} + \underset{\text{Hydrogen (nascent)}}{12H} = \underset{\text{Arsenium}}{As_4} + \underset{\text{Water}}{6H_2O}$$

$$\underset{\text{Arsenium}}{As_4} + \underset{\text{Hydrogen (nascent)}}{12H} = \underset{\text{Hydrogen arsenide}}{4AsH_3}$$

Hold a piece of glazed earthenware or porcelain (the lid of a porcelain crucible (*b*) if at hand) in the burning hydrogen jet; a brown spot of arsenium is deposited on the cold surface. Collect several of these deposits, and retain them for future comparison with antimony deposits similarly obtained. To ensure the conversion of the whole of the arsenic into hydrogen arsenide, it is advisable, towards the end of the operation, to add a few drops of solution of stannous chloride in hydrochloric acid to the generating-flask; this causes the precipitation of the arsenium in a state of very fine division, in which it is readily acted upon by the nascent hydrogen.

The separation of arsenium in the flame is due to the decomposition of the hydrogen arsenide by the heat. The cool porcelain at once condenses the arsenium, and thus prevents its oxidation to arsenious anhydride (which would otherwise take place at the outer edge of the flame).

Hold a small beaker (*c*), or wide test-tube, over the flame for a few minutes; a white film of arsenious anhydride, As_4O_6, will be deposited slowly, and may be further examined in contrast with the similarly produced film of antimonious oxide.

During these experiments the effect produced by the burning of the hydrogen arsenide on the colour of the hydrogen flame should be noted; the flame acquires a characteristic dull, livid, bluish tint.

Apply the flame of a gas-lamp to the middle of the hard glass delivery-tube (*d*, fig. 35); the hydrogen arsenide is decomposed as before, but the liberated arsenium condenses in the cool part of the tube, beyond the flame, as a dark metallic mirror. The tube may be removed and kept for comparison with an antimony deposit.

Note 1.—The zinc and sulphuric acid used for Marsh's test must be free from arsenium. Zinc, like copper, frequently contains arsenium as impurity. When a specimen, free from arsenium, is met with, it should be reserved for analytical experiments. Sulphuric acid, free from arsenium, can usually be purchased, but samples must always be tested as to their purity.

Note 2.—In delicate and important applications of Marsh's test, magnesium may be substituted for zinc with safety, arsenium not being found in magnesium. Magnesium in rods is convenient for this purpose. Both magnesium and zinc, if perfectly pure, interact with acids extremely slowly; but the addition of a very small quantity of chloroplatinic acid, at once promotes an abundant evolution of hydrogen. Platinum, however, has a tendency to hold back arsenium. According to Dyer, rod zinc has a similar tendency, while granulated zinc at once gives hydrogen arsenide.

Note 3.—Sulphuric acid, which is often used for drying gases, decomposes hydrogen arsenide. Calcium chloride is the appropriate desiccating agent for this gas.

Note 4.—The original apparatus proposed by Mr Marsh, a pharmacist, of Woolwich, in 1836, was a U-shaped tube, one limb of which was short, and closed by a stopcock, so that the whole of a small quantity of hydrogen arsenide could be collected, and afterwards examined at leisure.

Note 5.—On account of the exceedingly poisonous character of hydrogen arsenide, the preceding test and the next one should be conducted in a well-ventilated fume-cupboard.

4. *Fleitmann's Test.*—Generate hydrogen by heating a concentrated solution of caustic soda or potash and some pieces of zinc in a test-tube, to near the boiling point ($Zn + 2NaOH = H_2 + Na_2ZnO_2$, *see* p. 147). Add a drop of an arsenical solution. Now spread over the mouth of the tube a cap of filter-paper moistened with one drop of solution of silver nitrate. Again heat the tube, taking care that the liquid itself shall not spurt up on to the cap. A plug of cotton wool may even be placed in the mouth of the test-tube to arrest this spurting. The arsenical compound is reduced to arsenium, which unites with the hydrogen, as in Marsh's test; and the hydrogen arsenide passing up through the cap interacts with the silver nitrate, producing a purplish-black spot (of silver).

$$AsH_3 + 3H_2O + 6AgNO_3 = H_3AsO_3 + 6HNO_3 + 6Ag.$$

Note 1.—This reaction is valuable, since it enables the analyst quickly to distinguish arsenium in the presence of antimony. During the reduction of an antimony compound by nascent hydrogen in an acid solution, a portion of the antimony is converted into antimoniuretted hydrogen, SbH_3, which also acts upon silver nitrate; whereas if the reduction is carried out in an alkaline solution, antimoniuretted hydrogen is not formed, and hence the effect just described is not produced.

Note 2.—Aluminium answers as well as zinc for Fleitmann's test (Gatehouse), or magnesium may be used; or instead of zinc and alkali, sodium amalgam containing only a small proportion of sodium may be employed (Davy).

Note 3.—If the filter-paper cap is moistened with solution of mercuric chloride and then exposed to the action of hydrogen arsenide, a yellow stain, $AsHHg_2Cl_2$, results; becoming after a time brown, $AsHg_3Cl_3$, and then black, As_2Hg_3.

5. *Bettendorff's Test.*—To a solution of stannous chloride in concentrated hydrochloric acid add a very small quantity of any arsenical solution. Arsenium then separates, especially on the application of heat, producing a yellowish and then brownish colour, a greyish-brown turbidity, or even a sediment of grey-brown flocks, according to the quantity present. Much water prevents the reaction; and its presence must therefore be avoided as far as possible; indeed, a liquid saturated with hydrochloric acid gas gives the best results. The presence of arsenic in sulphuric or hydrochloric acid, or in tartar emetic, etc., may be detected by means of this test. Nitrates, such as bismuth oxynitrate, must first be heated with sulphuric acid to remove the nitric acid radical before applying this test for arsenium. The stannous salt is converted into stannic salt during the reaction.

The foregoing are the most important reactions of arsenium, whether existing in the arsenious or arsenic condition; of the following reactions 10 and 11 may be employed to distinguish arsenious and arsenic compounds from each other.

6. Through an acidulated arsenious solution pass hydrogen sulphide; a yellow precipitate of arsenious sulphide, As_2S_3, is at once produced. Add an alkali-metal hydroxide or hydrosulphide to a portion of the precipitate; it readily

dissolves. The precipitate consequently would not be produced on passing hydrogen sulphide through an alkaline arsenious solution.

When arsenious sulphide is dissolved in a solution of a hydrosulphide, a soluble meta-thiarsenite (*θεῖον, theion,* sulphur) is produced. Thus when ammonium hydrosulphide is used the solution contains ammonium meta-thiarsenite—

$$As_2S_3 + 2NH_4HS = 2NH_4AsS_2 + H_2S$$

When a hydroxide is used, a mixture of metarsenite and meta-thiarsenite is obtained—

$$2As_2S_3 + 4NaOH = NaAsO_2 + 3NaAsS_2 + 2H_2O$$

To another portion of the arsenious sulphide precipitate, well drained, add concentrated hydrochloric acid; it is insoluble—unlike antimonious sulphide. (Neither sulphide is soluble in dilute hydrochloric acid.)

Note 1.—A yellow sulphide is also produced in an acid solution of a cadmium salt by the action of hydrogen sulphide, but this sulphide is insoluble in alkaline liquids. Under certain circumstances tin, too, yields a yellow sulphide, but tin is otherwise easily distinguished.

Note 2.—A trace of arsenious sulphide is sometimes met with in the sulphur distilled from arsenical pyrites. It may be detected by digesting the sulphur in solution of ammonia, filtering, and evaporating to dryness; a yellow residue of arsenious sulphide is obtained if that substance be present.

7. Through an acidulated solution of arsenic acid, or any other arsenate, pass a rapid current of hydrogen sulphide; a yellow precipitate of arsenic sulphide, As_2S_5, is produced, but precipitation takes place very slowly in cold solutions. Brauner and Tornicek state that by a slow current the arsenic acid is gradually reduced to arsenious acid, and a yellow precipitate is formed which consists of arsenious sulphide mixed with sulphur. The reaction is more rapid if the solution be warmed. The precipitate is soluble in alkali-metal hydroxides and hydrosulphides. When it is dissolved

a hydrosulphide the solution contains a thiarsenate, while a ydroxide produces a mixture of arsenate and thiarsenate.

8. To an aqueous solution of arsenious anhydride add two r three drops of solution of cupric sulphate, and then autiously add dilute solution of ammonia, drop by drop, until green precipitate is obtained. The production of this recipitate is characteristic. To a portion of the mixture dd an acid; the precipitate dissolves. To another portion dd an alkali; the precipitate dissolves. The solubility of e precipitate in both acid and alkali shows the advantage f testing a suspected arsenical solution by means of litmus-aper before applying this reaction, and if found to be acid, autiously adding alkali, or if alkaline, adding acid, till eutrality is obtained; or a special reagent—copper am-onio-sulphate—may be used. (*See* note to reaction 11.)

The precipitate consists of cupric arsenite, $CuHAsO_3$, or *cheele's Green.* In the pure state, or mixed with cupric cetate or, occasionally, with cupric carbonate, it is used as pigment under different names, such as Brunswick Green nd Schweinfurth Green, by painters and others.

9. Apply the test just described to a solution of arsenic cid or other arsenate; a somewhat similarly coloured pre-ipitate of cupric arsenate is obtained.

10. Repeat reaction 8, substituting silver nitrate for upric sulphate: in this case a *yellow* precipitate of silver rsenite, Ag_3AsO_3, is produced, also soluble in acids and lkalies.

11. Apply the silver nitrate test of the preceding re-ction to a solution of arsenic acid or other arsenate; a brown recipitate of silver arsenate, Ag_3AsO_4, is formed.

Copper and Silver Reagents for Arsenium.—The last four eactions may be performed with increased delicacy and ertainty of result if the copper and silver reagents be pre-iously prepared in the following manner:—To a solution of ure cupric sulphate (about 1 part in 20 of water) add am-monia until the blue precipitate at first formed is nearly, but not quite, redissolved; filter and preserve the liquid as an arsenium reagent, labelling it *Solution of copper ammonio-sulphate* (B.P.). Treat solution of silver nitrate (about 1 part in 40) in the same way, and label it *Solution of silver ammonio-nitrate* (B.P.). The composition of these two salts will be referred to subsequently.

Arsenious and Arsenic Compounds.—While many reagents may be used for the detection of arsenium, only the behaviour with silver nitrate will immediately and distinctly indicate in which state the arsenium exists; for the two sulphides and the two copper precipitates, though differing in composition, resemble each other in appearance, whereas the two silver precipitates differ in colour as well as in composition.

Soluble arsenates give precipitates of insoluble arsenates on the addition of solutions of salts of barium, calcium, zinc, and other metals.

Arsenium, when it exists as arsenic acid or other arsenate, does not rapidly respond to the test with hydrogen sulphide or nascent hydrogen. Hence, if its presence, as arsenate, is suspected, the liquid under examination should be warmed with a little sulphurous acid—or treated with hydrochloric acid until slightly acid and then with solution of sodium thiosulphate—before the addition of hydrogen sulphide.

Antidote in cases of Arsenical Poisoning.—The most effective antidote in these cases is recently precipitated moist ferric hydroxide, administered as soon as possible. It is perhaps best administered in the form of the mixture obtained by adding sodium carbonate to a solution of ferric chloride (*Liquor Ferri Perchloridi,* B.P.) two to three ounces of the latter to about one ounce of the crystals of the former. Instead of the sodium carbonate, about a quarter of an ounce of calcined magnesia (*Magnesia,* B.P.) may be used. These quantities will render at least 10 grains of arsenious anhydride insoluble. Emetics should also be given, and the stomach-pump, or a common indiarubber tube, used as a siphon, be applied as quickly as possible.

The above statements regarding the antidote for arsenical oisoning may be verified by mixing the various substances gether, filtering, and proving the absence of arsenium in e filtrate by applying some of the foregoing tests.

Mode of Action of the Antidote.—The action of the sodium rbonate or the magnesia is to precipitate ferric hydroxide, e(OH)$_3$—sodium chloride, NaCl, or magnesium chloride, gCl$_2$, being formed, either of which is at least harmless, if ot beneficial, under the circumstances. The interaction etween ferric hydroxide and arsenious acid results in the rmation of insoluble ferrous arsenate. (*See* also p. 171.)

QUESTIONS AND EXERCISES

What is the formula of a molecule of arsenium?—In what form oes arsenium occur in nature?—Describe the characters of white senic. Name the official preparations of arsenium.—What com- ounds of arsenium are contained in *Liquor Arsenicalis*, B.P., and *quor Arsenici Hydrochloricus*, B.P.?—By what method may arsenic reduced to arsenium?—Give the formulæ of arsenious and arsenic ids and anhydrides.—Explain, by equations, the reactions which cur in converting arsenic into sodium arsenate.—Why is anhy- ous instead of crystallized sodium arsenate employed officially?— the preparation of iron arsenate from ferrous sulphate and sodium senate, why is sodium bicarbonate included? Describe the mani- ulations necessary to obtain arsenic in its characteristic crystalline rm.—How is Reinsch's test for arsenium applied, and under what cumstances may its indications be fallacious?—Give the details of arsh's test for arsenium, and the precautions to be observed. Ex- ain the reactions by diagrams.—What peculiar value has Fleitmann's st for arsenium?—Describe the conditions under which hydrogen lphide becomes a trustworthy test for arsenium.—How may a trace arsenious sulphide be detected in sulphur?—How are salts of copper d silver applied as reagents for the detection of arsenium?—How e arsenites distinguished from arsenates?—Mention the best antidote cases of arsenical poisoning; describe the process by which it may most quickly prepared, and explain its action.

ANTIMONY: Sb (Stibium). Atomic weight, 119

Occurrence, etc.—Antimony occurs in nature chiefly as ntimonious sulphide, Sb$_2$S$_3$, *stibnite*. The crude or *black ntimony* of pharmacy is this native sulphide freed from npurities by fusion: it has a striated, crystalline, lustrous acture; subsequently powdered and, if it contains any soluble salt of arsenium, the latter removed by digestion in solution of ammonia, it forms the greyish-black crystalline *Antimonium Nigrum Purificatum,* B.P. The metal is obtained from the sulphide by roasting, the resulting oxide being reduced with charcoal and sodium carbonate. The resulting scoria is known as *crocus of antimony* or *glass of antimony.* Antimony is also obtained from the native sulphide by heating it with iron, ferrous sulphide being formed at the same time. Metallic antimony is an important constituent of *type-metal, Britannia metal,* and the best varieties of *pewter.* The old *pocula emetica,* or everlasting emetic cups, were made of antimony; wine kept in them for a day or two was said to have acquired an emetic quality. The metal is not used in making official antimony preparations, the sulphide alone being, directly or indirectly, employed for this purpose.

Antimony has very close chemical analogies with arsenium. Like arsenium, it unites with iodine to form a tri-iodide (SbI_3). A bromide, $SbBr_3$, also is known.

Antimonious and Antimonic Chlorides

Experiment 1.—Boil about half an ounce of antimonious sulphide with four or five times its weight of hydrochloric acid in a dish placed in a fume-cupboard or in the open-air; hydrogen sulphide is evolved and solution of antimonious chloride, $SbCl_3$, is obtained.

$$\underset{\text{Antimonious sulphide}}{Sb_2S_3} + \underset{\text{Hydrochloric acid}}{6HCl} = \underset{\text{Antimonious chloride}}{2SbCl_3} + \underset{\text{Hydrogen sulphide}}{3H_2S}$$

This solution, cleared by subsidence, is what is commonly known as *butter of antimony.* If pure sulphide has been used in its preparation, the liquid is nearly colourless; but much of that met with in veterinary pharmacy is simply a by-product in the generation of hydrogen sulphide from native ferruginous antimonious sulphide and hydrochloric acid, and is more or less brown from the presence of ferric chloride. It not infrequently darkens in colour on keeping; this is due to absorption of oxygen from the air, and conversion of light-coloured ferrous into dark-brown ferric chloride or oxychloride. It is a powerful caustic.

True *butter of antimony,* $SbCl_3$, is obtained on evaporating the above solution to a small volume, and distilling the residue.

he butter condenses as a white crystalline semi-transparent ass in the neck of the retort ; at the close of the operation may be melted and allowed to flow into a bottle, which ould be well stoppered. It is highly corrosive.

Antimony pentachloride or *antimonic chloride*, $SbCl_5$, is a ming liquid, obtained by passing chlorine over the ichloride.

Antimonious Oxychloride

Experiment 2.—Boil the solution of antimonious chloride roduced in experiment 1, and pour it into several ounces water ; a white precipitate of antimonious oxychloride, $b_4O_5Cl_2$, is produced, some antimonious chloride remaining the supernatant acid liquid.

This precipitate is the substance formerly known as *ulvis Algarothi, pulvis angelicus,* or *mercurius vitæ.* It varies mewhat in composition, according to the amount of water ith which the chloride may be mixed ; but, on standing der water, gradually becomes crystalline, and has the com- sition given above.

$$\underset{\text{Antimonious chloride}}{4SbCl_3} + \underset{\text{Water}}{5H_2O} = \underset{\text{Antimonious oxychloride}}{Sb_4O_5Cl_2} + \underset{\text{Hydrochloric acid}}{10HCl}$$

Antimonious Oxide

Experiment 3.—Wash the precipitate obtained in experi- ent 2, thoroughly with water, by decantation (*see* p. 122), nd add solution of sodium carbonate ; the oxychloride is composed, and antimonious oxide, Sb_4O_6 (*Antimonii Oxidum,* .P.), is produced. The latter is of a light buff or greyish- hite colour, or quite white if absolutely free from iron, soluble in water, soluble in hydrochloric acid, fusible at a w red heat. The moist antimonious oxide may be well ashed and employed for experiment 4, or it may be dried a water-bath. At temperatures above 212° F. (100° C.) it sorbs oxygen and other antimony oxides are formed. The resence of the latter may be detected on boiling the powder solution of acid potassium tartrate, in which antimonious xide, Sb_4O_6, is soluble, but *antimonic anhydride*, Sb_2O_5, and antimony tetroxide, Sb_2O_4 or Sb_4O_8 (Sb_2O_3, Sb_2O_5), are insoluble.

$$\underset{\text{Antimonious oxychloride}}{Sb_4O_5Cl_2} + \underset{\text{Sodium carbonate}}{Na_2CO_3} = \underset{\text{Antimonious oxide}}{Sb_4O_6} + \underset{\text{Sodium chloride}}{2NaCl} + \underset{\text{Carbonic anhydride}}{CO_2}$$

Antimonious oxide, besides its use in the preparation of tartar emetic (*see* below), is mixed with twice its weight of calcium phosphate (purified bone-earth) to form *Pulvis Antimonialis*, B.P., or "James's Powder."

The higher antimony oxide, Sb_2O_5, termed *antimonic oxide* or *anhydride*, corresponding to arsenic anhydride, is obtained by decomposing the pentachloride with water, or by boiling metallic antimony with nitric acid. The variety obtained from the chloride differs in saturating power from that obtained from the metal, and is termed metantimonic acid.

Tartar Emetic

Experiment 4.—Mix the moist antimonious oxide obtained in experiment 3, with about an equal quantity of acid potassium tartrate (6 parts of the latter to 5 of the dry oxide) and sufficient water to form a paste; set aside for a day to facilitate complete combination; boil the product with water, and filter; the resulting liquid contains antimony potassio-tartrate, tartarated antimony, or tartar emetic (emetic, from ἐμέω, *emeō*, I vomit) $KSbOC_4H_4O_6$.

$$\underset{\text{Acid potassium tartrate}}{4KHC_4H_4O_6} + \underset{\text{Antimonious oxide}}{Sb_4O_6} = \underset{\text{Tartar emetic}}{4KSbOC_4H_4O_6} + \underset{\text{Water}}{2H_2O}$$

On evaporation, the salt is obtained "in colourless transparent crystals exhibiting triangular facets." These contain water of crystallization, and are represented by the formula $[K(SbO)C_4H_4O_6]_2$, H_2O (*Antimonium Tartaratum*, B.P.).

Tartar emetic is very commonly represented (as above) as potassium antimonyl tartrate ($SbO' =$ antimonyl). It seems almost certain, however, that it is really the potassium salt of tartrantimonious acid, $HSbC_4H_4O_7$, in which antimony is present as a part of the acid radical. A solution of this acid (which is very unstable), also the barium and several other salts, have been obtained.

Tartar emetic is soluble in water, and slightly so in 60 per cent. alcohol. A solution in sherry forms the official *Vinum Antimoniale,* B.P.

Sulphurated Antimony and other Antimony Oxysulphides

Experiment 5.—Boil a few grains of antimonious sulphide and of sulphur with solution of caustic soda in a test-tube, and filter (or on a larger scale, 10 ounces of antimonious sulphide, 10 of sulphur, and 5 of caustic soda, for 2 hours, frequently stirring, and occasionally replacing water lost by evaporation). Into the filtrate, while still hot, stir dilute sulphuric acid until the liquid is slightly acid to test-paper; an orange-red precipitate is produced. Prepared with official quantities, this precipitate, when filtered, washed, and dried on a water-bath, is sulphurated antimony (*Antimonium Sulphuratum,* B.P.). It is a mixture of antimony pentasulphide, Sb_2S_5, with a little oxide (Sb_4O_6, or possibly Sb_2O_5) and some free sulphur. The oxide results from the interaction of antimonious sulphide and caustic soda in the presence of air.

This is one of the many varieties of *mineral kermes,* so alled from their similarity in colour to the *insect kermes.* *Kermes* is the name, now obsolete, of the *Coccus Ilicis,* a sort of cochineal-insect, full of reddish juice, and used since the arliest times for dyeing. The term *mineral kermes* was apparently applied originally to the amorphous or precipitated orange antimonious sulphide, Sb_2S_3. It afterwards included any mixture of this with oxysulphide and pentasulphide. A brownish-red variety may be prepared without the addition of any free sulphur; the colour of the precipitate is then ffected by the temperature as well as by the state of dilution f the alkaline liquid when the acid is added. When this lkaline liquid is boiled in contact with air, oxygen is absorbed and unites with some of the antimony, displacing ulphur which, in turn, converts some antimony trisulphide nto pentasulphide. *Kermes* may be formed by fusion as well s by boiling the components in aqueous solution.

Explanation of processes.—The antimony sulphides and xides, like those of arsenium, interact with the sulphides and hydroxides of certain metals to form salts which are more or less soluble in water. Thus when antimonious sulphide is dissolved in hot solution of caustic soda, sodium metantimonite, $NaSbO_2$, and meta-thiantimonite, $NaSbS_2$, are formed: in the presence of sulphur, sodium metantimonate, $NaSbO_3$, and sodium thiantimonate are produced, the former of which is sparingly soluble.

$$\underset{\substack{\text{Antimonious}\\\text{sulphide}}}{2Sb_2S_3} + \underset{\substack{\text{Caustic}\\\text{soda}}}{4NaOH} = \underset{\substack{\text{Sodium}\\\text{metantimonite}}}{NaSbO_2} + \underset{\substack{\text{Sodium}\\\text{meta-thiantimonite}}}{3NaSbS_2} + \underset{\text{Water}}{2H_2O}$$

$$\underset{\substack{\text{Antimonious}\\\text{sulphide}}}{4Sb_2S_3} + \underset{\text{Sulphur}}{8S} + \underset{\substack{\text{Caustic}\\\text{soda}}}{18NaOH} = \underset{\substack{\text{Sodium}\\\text{metantimonate}}}{3NaSbO_3} + \underset{\substack{\text{Sodium}\\\text{thiantimonate}}}{5Na_3SbS_4} + \underset{\text{Water}}{9H_2O}$$

The salts so formed in hot solutions are not all stable in cold solutions, and antimony oxides, or sulphides, or both, are deposited when the hot solutions cool. Thus sodium meta-thiantimonite decomposes yielding sodium ortho-thiantimonite, Na_3SbS_3, and a deposit of antimonious sulphide, Sb_2S_3:

$$3NaSbS_2 = Na_3SbS_3 + Sb_2S_3$$

In the preparation of kermes, therefore, the acid should be added to the solution obtained on boiling up the necessary ingredients, before any precipitate has separated (that is, before the solution is cool), if uniformity of product is desired.

$$\underset{\substack{\text{Sodium meta-}\\\text{thiantimonite}}}{2NaSbS_2} + \underset{\substack{\text{Sulphuric}\\\text{acid}}}{H_2SO_4} = \underset{\substack{\text{Sodium}\\\text{sulphate}}}{Na_2SO_4} + \underset{\substack{\text{Antimonious}\\\text{sulphide}}}{Sb_2S_3} + \underset{\substack{\text{Hydrogen}\\\text{sulphide}}}{H_2S}$$

$$\underset{\substack{\text{Sodium}\\\text{metantimonite}}}{4NaSbO_2} + \underset{\substack{\text{Sulphuric}\\\text{acid}}}{2H_2SO_4} = \underset{\substack{\text{Sodium}\\\text{sulphate}}}{2Na_2SO_4} + \underset{\substack{\text{Antimonious}\\\text{oxide}}}{Sb_4O_6} + \underset{\text{Water}}{2H_2O}$$

$$\underset{\substack{\text{Sodium}\\\text{thiantimonate}}}{2Na_3SbS_4} + \underset{\substack{\text{Sulphuric}\\\text{acid}}}{3H_2SO_4} = \underset{\substack{\text{Sodium}\\\text{sulphate}}}{3Na_2SO_4} + \underset{\substack{\text{Antimonic}\\\text{sulphide}}}{Sb_2S_5} + \underset{\substack{\text{Hydrogen}\\\text{sulphide}}}{3H_2S}$$

$$\underset{\substack{\text{Sodium}\\\text{metantimonate}}}{2NaSbO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid}}}{H_2SO_4} = \underset{\substack{\text{Sodium}\\\text{sulphate}}}{Na_2SO_4} + \underset{\substack{\text{Antimonic}\\\text{oxide}}}{Sb_2O_5} + \underset{\text{Water}}{H_2O}$$

The oxides and sulphides indicated in these equations, are all precipitated when the acid is added, and form the varieties of *kermes*.

Analytical Reactions of Antimonious Salts.

1. Through an acidified antimonious solution pass hydrogen sulphide; an orange precipitate of amorphous antimonious

sulphide, Sb_2S_3, is produced. It has the same composition as the crystalline black sulphide into which, indeed, when dried, it is quickly converted by heat. Like arsenious sulphide, it is soluble in solutions of alkali-metal hydrosulphides and hydroxides. Collect a portion on a filter and, when well drained, add concentrated hydrochloric acid; it dissolves—unlike arsenious sulphide.

Antimonic sulphide, Sb_2S_5, corresponding to arsenic sulphide, As_2S_5, is known. It is formed on passing hydrogen sulphide through an acidulated solution of antimonic chloride, $SbCl_5$, or, less pure, on boiling black antimonious sulphide and sulphur with a caustic alkali, and decomposing the resulting filtered liquid by means of an acid.

2. Dilute two or three drops of a solution of antimonious chloride with water; a white precipitate of antimonious oxychloride is produced (*see* experiment 2, p. 207). The production of a precipitate in these circumstances distinguishes antimony from arsenium, but the reaction is not capable of being applied as a delicate discriminating test in analysis. Add a sufficient quantity of hydrochloric acid to dissolve the precipitate, and boil a piece of copper in the solution, as directed in the corresponding test for arsenium (reaction 2, p. 196); antimony is deposited on the copper. Wash, dry, and heat the copper in a test-tube as there described; the antimony, like the arsenium, is volatilized off the copper and oxidized, and the white oxide condenses on the side of the tube; but the sublimate, from its low degree of volatility, condenses close to the copper; moreover, it is generally non-crystalline, rarely in acicular or octahedral crystals.

Shake out the copper and boil water in the tube for several minutes. Do the same with the arsenical sublimate similarly obtained. The latter slowly dissolves, and may be recognised in the solution by means of silver ammonio-nitrate; the antimonial sublimate is insoluble.

3. Perform the operations described under Marsh's test for arsenium (reaction 3, p. 197), placing the apparatus

in a well-ventilated fume-cupboard and carefully observing all the details there mentioned, but using a few drops of solution of antimonious chloride or of tartar emetic instead of the arsenical solution. Antimony hydride, antimoniuretted hydrogen, or hydrogen antimonide, SbH_3, is formed and may be decomposed in the same way as arsenium hydride.

To one of the arsenium spots on the porcelain lid (p. 199) add a drop of a dilute solution of bleaching-powder; it quickly dissolves. Do the same with an antimony spot; it is unaffected. Heat more quickly causes the volatilization of an arsenium than of an antimony spot; ammonium hydrosulphide more readily dissolves the antimony than the arsenium.

Boil water for several minutes in the beaker or wide test-tube containing the arsenical sublimate (p. 199); it slowly dissolves, and may be recognised in the solution by the yellow precipitate given on the addition of solution of silver ammonio-nitrate. The antimonial sublimate, similarly treated, does not dissolve.

Pass a slow current of hydrogen sulphide through the delivery-tube removed from the hydrogen-apparatus (p. 199), and when the air has been expelled from the tube, gently heat that portion containing the deposit of arsenium; the latter will be converted into a *yellow* sublimate of arsenious sulphide. Remove the tube from the hydrogen-sulphide apparatus, and repeat the experiment with an antimony deposit; it is converted into *orange* antimonious sulphide, which, moreover, owing to inferior volatility, condenses nearer to the flame than the arsenious sulphide does.

Pass dry hydrochloric acid gas through the two delivery-tubes. This is accomplished by adapting first one tube and then the other, by means of a cork, to a test-tube containing a few lumps of common salt, upon which a little sulphuric acid is poured prior to the insertion of the cork. The antimonious sulphide dissolves and disappears; the arsenious sulphide is unaffected.

Antidote in cases of Antimonial Poisoning.—The introduction of poisonous doses of antimonial compounds into the stomach is fortunately quickly followed by vomiting. If vomiting has not occurred, or apparently to an insufficient extent, tannic acid in any form may be administered (infusion of tea, nutgalls, cinchona, oak-bark, or other astringent solutions or tinctures), an insoluble antimony tannate being formed, and absorption of the poison being thereby somewhat retarded. The stomach-pump or stomach-siphon must be applied as quickly as possible.

Recently precipitated moist ferric hydroxide is also, according to T. and H. Smith, a complete precipitant of antimony from its solutions, the chemical action being probably, they say, similar to that which takes place between ferric hydroxide and arsenious anhydride. It may be given in the form of a mixture of ferric chloride with either sodium carbonate or other soluble carbonate or bicarbonate, or with magnesia.

These statements may be verified by mixing together the various substances, filtering and testing the filtrate for antimony in the usual manner.

QUESTIONS AND EXERCISES

What is the composition and source of "*Black Antimony*"?—In what alloys is metallic antimony a characteristic ingredient?—What is the quantivalence of antimony as far as indicated by the formulæ of the official preparations?—Show by an equation how "Butter of Antimony" is prepared.—Write out equations or diagrams expressive of the reactions which occur in converting antimonious chloride into oxide.—What is the formula of Tartar Emetic?—Explain by aid of equations the preparation of *Antimonium Sulphuratum*, B.P.—Give a comparative statement of the tests for arsenium and antimony.—How is antimony detected in the presence of arsenium?

TIN: Sn. Atomic weight, 118·2

Occurrence, etc.—The chief ore of tin is stannic oxide, SnO_2, occurring in veins under the name of *tinstone*, or in alluvial deposits as *stream-tin*. The oldest mines are those of

Cornwall. Much tin is now imported from Australia. The metal is obtained by reducing the roasted and washed ore by means of charcoal or anthracite* coal at a high temperature, and is purified by slowly heating, when the pure tin, fusing first, is run off, a somewhat less fusible alloy of tin, with small quantities of arsenium, copper, iron, or lead remaining. The latter is known as *block tin;* the former heated till brittle and then hammered or let fall from a height splits into prismatic fragments resembling those of starch or of columnar basalt, and is named *dropped* or *grain tin.* Good tin on being bent emits a crackling noise, which is termed the "cry" of tin, and is caused by the friction of its crystalline particles on each other.

Uses.—Tin is an important constituent of such alloys as pewter, Britannia metal, solder, speculum-metal, bell-metal, gun-metal, and bronze. It is very ductile, and may be rolled into plates, or into leaves known as *tin foil,* varying from $\frac{1}{250}$ to $\frac{1}{1000}$ of an inch in thickness. Common tin foil, however, usually contains a large proportion of lead. The reflecting surface of *looking-glasses* was formerly always an amalgam of tin and mercury, produced by carefully sliding a plate of glass over a sheet of tin foil on which mercury had been rubbed, and then excess of mercury had been poured—but pure silver, deposited from a solution, is now largely employed. *Pins* are made of brass or iron wire on which tin is deposited. *Tin plate,* of which common utensils are made, is iron alloyed with tin by dipping acid-cleansed sheet-iron which has been immersed in melted tallow, into vessels containing melted tin, and subsequently heating it in a bath of melted tallow, which, by preventing oxidation, enables the tin more completely to alloy with the iron. *Tin tacks* are in reality tinned iron tacks. Tin may be granulated by melting it and triturating it briskly in a hot mortar; or by shaking melted tin in a box, on the inner sides of which chalk has been rubbed. It may also be obtained in thin bell-shaped or corrugated fragments (Tin, B.P.), by melting it in a ladle, and, as soon as it is fluid, pouring it from the height of a few feet into water. Powdered tin has been used medicinally as a mechanical irritant to promote expulsion of worms.*

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* *Anthracite* (from ἄνθραξ, *anthrax*, a burning coal), or *stone coal*, differs from the ordinary *bituminous* or *caking coal* in containing less volatile matter, and, therefore, in burning without flame. It gives a higher temperature, and from its non-caking properties, is, in furnace operations, more manageable than bituminous coal.

Tin forms two sets of compounds which are called stannous and stannic, respectively. They correspond to the two oxides, SnO and SnO_2.

Stannous Chloride

Experiment 1.—Warm a fragment of tin with hydrochloric acid ; hydrogen escapes and a solution of stannous chloride, $SnCl_2$, is formed. It may be retained for future experiments.

The solution obtained by dissolving tin in hot dilute hydrochloric acid (some undissolved tin being kept in the liquid) constitutes the "Solution of Stannous Chloride," B.P.

Solid Stannous Chloride.—By evaporation of the above solution, stannous chloride is obtainable in crystals, $SnCl_2$, $2H_2O$. It is a powerful reducing agent, even a dilute solution precipitating gold, silver, and mercury from their solutions, converting ferric and cupric into ferrous and cuprous salts, and partially deoxidizing arsenic, manganic, and chromic acids. It absorbs oxygen from the air, and is decomposed when added to a large quantity of water unless some acid be present. It is used as a mordant in dyeing and calico-printing.

Stannic Chloride

Experiment 2.—Pass chlorine through a portion of the solution of the stannous chloride of the preceding experiment ; a solution of stannic chloride, $SnCl_4$, is formed. Or add hydrochloric acid to the stannous solution, boil, and, in a fume-cupboard, slowly drop in nitric acid until no more fumes are evolved ; again stannic chloride results. Reserve the solutions for subsequent experiments.

Stannic Oxide, or Anhydride, and Stannates

Experiment 3.—Boil a fragment of tin with nitric acid, evaporate to dryness, and strongly ignite the residue ; light buff-tinted stannic anhydride, SnO_2, is produced. Heat the stannic anhydride with excess of solid caustic potash or soda; stannate of the alkali-metal (K_2SnO_3 or Na_2SnO_3) results. Dissolve the stannate in water, and add hydrochloric acid; white gelatinous *stannic acid*, H_2SnO_3, is precipitated.

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* The hairs of the pod of *Kiwach* (Hindustani) or *Cowhage* (*Mucuna pruriens*) (P.I.) is almost the only other medicine (excluding diluents and dentifrices) which acts in such a directly mechanical manner.

Stannic acid is also obtained on adding a solution of a caustic alkali to solution of stannic chloride; it is soluble in excess of acid or of caustic alkali. The precipitate in this case appears to correspond to the formula H_4SnO_4, but it easily loses water and becomes H_2SnO_3.

$$SnCl_4 + 4KOH = H_4SnO_4 + 4KCl$$
$$Sn(OH)_4 = H_2O + H_2SnO_3$$

The product of the action of nitric acid on tin is also an acid, but it is different from ordinary stannic acid inasmuch as it is converted by hydrochloric acid into metastannic chloride, which is insoluble in moderately concentrated hydrochloric acid although soluble in water. It is called *metastannic acid*, and its molecule probably has the composition expressed by the formula $H_{20}Sn_5O_{20}$. If dried over sulphuric acid, or at 100° C., it becomes $H_{10}Sn_5O_{15}$ (sodium salt, $H_8Na_2Sn_5O_{15}$). This latter substance is also produced by gently heating the acid resulting from the interaction of caustic potash and stannic chloride.

$$5H_4SnO_4 = H_{10}Sn_5O_{15} + 5H_2O$$

Both acids yield buff-coloured stannic oxide or anhydride, SnO_2, when strongly heated. The latter is employed in polishing plate under the name of *putty powder*. *Sodium stannate*, $Na_2SnO_3,3H_2O$, is used as a mordant by dyers and calico-printers under the name of *tin prepare-liquor*.

Analytical Reactions of Tin Compounds.

Stannous or Stannic Salts.—Heat any solid compound of tin with a mixture of potassium cyanide and sodium carbonate on charcoal in the inner flame of the blowpipe. Hard globules of tin separate which, when cut by a knife, exhibit a characteristic bright white surface.

Reactions of Stannous Salts.

1. Through a dilute solution of a stannous salt (stannous chloride, for example) pass hydrogen sulphide; a brown precipitate of stannous sulphide, SnS, results. Pour off the supernatant liquid, add solution of ammonia to the moist precipitate (to neutralize acid), and then ammonium hydrosulphide solution; the precipitate is at least partially dissolved. The addition of some sulphur and the application of heat may be necessary to effect complete solution.

Aqueous solution of ammonium hydrosulphide becomes yellow when a day or two old, and then contains excess of sulphur, some of that element having become displaced by oxygen absorbed from the air. As a consequence of this (or by the aid of the added sulphur), the stannous sulphide, SnS, takes up sulphur and dissolves to form ammonium thiostannate. From this solution yellow stannic sulphide (usually mixed with sulphur) is precipitated by the addition of excess of an acid.

$$2SnS + 4NH_4HS + S_2 = 2(NH_4)_2SnS_3 + 2H_2S$$
$$(NH_4)_2SnS_3 + 2HCl = 2NH_4Cl + H_2S + SnS_2$$

2. To a solution of a stannous salt add solution of caustic potash or caustic soda; a white precipitate of stannous hydroxide, $Sn(OH)_2$, is produced. Add excess of the alkali; the precipitate dissolves. Boil the solution; some of the tin is reprecipitated as blackish stannous oxide, SnO. Ammonia gives a similar white precipitate, insoluble in excess. The alkali-metal carbonates do the same, carbonic anhydride escaping.

Reactions of Stannic Salts.

1. Through a solution of a stannic salt (stannic chloride, for example) pass hydrogen sulphide; a yellow precipitate of stannic sulphide, SnS_2, results. Pour off the supernatant liquid, and to the moist precipitate add ammonia (to neutralize acid), and then ammonium hydrosulphide; the precipitate dissolves.

Note.—In this reaction the presence of much hydrochloric acid must be avoided, and the formation of the precipitate is facilitated if the solution be warmed. Stannic sulphide, like the arsenium and antimony sulphides, dissolves in solutions of alkali-metal sulphides or hydrosulphides, with formation of definite crystallizable *thiostannates* (M_2SnS_3).

Anhydrous stannic sulphide, prepared by sublimation, has a yellow or orange lustrous appearance, and is known as *mosaic gold.* It was formerly used by decorators as *bronzing-powder,* but the latter now usually consists of powdered *bronze-leaf.*

2. To a solution of a stannic salt add caustic potash or caustic soda; a white precipitate of stannic acid, H_2SnO_3, is produced. Add excess of the alkali; the precipitate dissolves. Boil the mixture; no reprecipitation occurs—a reaction by means of which stannic may be distinguished from stannous salts.

Solution of ammonia gives a similar precipitate slowly soluble in excess. Potassium and sodium carbonates do the same, carbonic anhydride escaping; after a time the stannic salt is again deposited, probably as potassium or sodium stannate. Ammonium carbonate and all the bicarbonates give a precipitate of stannic acid, insoluble in excess.

Separation of Antimony and Tin.—If a piece of iron wire be placed in the acid (HCl) solution of the two metals, a black precipitate of antimony is formed, and the tin is reduced to the stannous condition; the latter may be detected by the addition of mercuric chloride solution, when a white precipitate of mercurous chloride is produced.

$$2HgCl_2 + SnCl_2 = SnCl_4 + 2HgCl$$

Antidotes.—In cases of poisoning by tin salts (*e.g.*, dyers' tin-liquor), solution of ammonium carbonate should be given; and white of egg is also said to form an insoluble precipitate. Vomiting should be induced, and the stomach-pump, or stomach-siphon, applied.

GOLD: Au. Atomic weight, 195·7

Occurrence, etc.—Gold occurs in the free state in nature, occasionally in nodules or *nuggets,* but in alluvial deposits commonly in a finer state of division termed *gold dust.* Gold separated from sand, crushed quartz, or other earthy matter ith which it may be associated, by agitation with water, when e gold, from its relatively greater specific gravity, falls to e bottom of the vessel first, the greater part of the lighter ineral matter being carried away by the water. From the ch sediment the gold is dissolved out by mercury; the amal- am is filtered and afterwards distilled, when the mercury latilizes and gold remains. The amalgamation may be cilitated by the use of sodium, as described under silver. rom even the poorest ores gold may be dissolved by solution potassium cyanide in presence of air. (*See* Faraday on gold af, 1857.) $8KCN + 4Au + O_2 + 2H_2O = 4KAu(CN)_2 + 4KOH$.

Pure gold is too soft for use in the form of coins for general rculation. *Gold coin* is usually an alloy of copper and gold, aat of Great Britain containing 1 of the former to 11 of the tter, or $8\frac{1}{3}$ per cent. of copper; that of France, Germany, nd the United States contains about 10 per cent. of copper. ustralian gold coins contain silver instead of copper as alloy. *ewellers' gold* varies in quality, every 24 parts containing 18, 5, 12, or 9 parts of gold, these alloys being technically rmed 18, 15, 12, or 9 *carat fine*, the reckoning being in ne old "parts per 24," instead of the more usual parts per ent. Articles made of the better qualities are usually amped by authority. Trinkets of inferior intrinsic worth re often thinly coated with pure gold by electro-deposition r otherwise. The so-called *mystery gold* is an alloy of about part platinum and 2 parts copper with a little silver. It esists the action of concentrated nitric acid. The action of qua regia and then ammonia reveals the presence of copper n it. *Gold leaf* is nearly pure gold ($1\frac{1}{2}$ to 4 per cent. of lver or copper, according to the lighter or darker tint quired) passed between rollers till it is about $\frac{1}{800}$ of an nch in thickness and then hammered between sheets of nimal membrane, termed gold-beaters' skin, and calf-skin ellum, till it is reduced to $\frac{1}{160000}$ or $\frac{1}{200000}$ of an inch in hickness. It may even be hammered till 280000 leaves ould be required to form a pile an inch thick.

Gold Coinage.—The weight of gold is expressed in this ountry in ounces, and decimal parts of an ounce, troy; and he metal is always taken to be of standard fineness (11 gold nd 1 alloy) unless otherwise described. The degree of fine- ess of gold, as ascertained by assay, is expressed decimally, fine pure gold being taken as unity, or 1·000. Thus gold of British standard is said to be 0·9166 fine, of French standard 0·900 fine. The legal weight of the sovereign is 0·2568 ounce of standard gold, or 123·274 grains; the weight coming from one pound of standard gold (5760 grains) being coined into 44½ guineas. Gold coins are legal tender to any amount, provided that the weight of each sovereign does not fall below 122·5 grains, or in the case of a half-sovereign 61·125 grains; these are the "least current" weights of the coins.

Experiment.—Place a fragment of gold (*e.g.*, gold leaf) in ten to twenty drops of aqua regia (a mixture of three parts of nitric and four or five of hydrochloric acids), and set aside in a warm place (in a fume-cupboard); a solution of chlorauric acid, $HAuCl_4$ (formerly regarded as a solution of gold trichloride or auric chloride, $AuCl_3$), results. Evaporate nearly to dryness to remove most of the excess of acid, dilute with water, and retain the solution for subsequent experiments. Such a solution is official (Solution of Auric Chloride, B.P.). Chlorauric acid is very deliquescent. Sodium chloraurate, $NaAuCl_4$, is a readily crystallizable salt.

This reaction is of analytical interest; for in examining a substance suspected to be or to contain metallic gold, solution would have to be effected in the above way before reagents could be applied, as gold is insoluble in hydrochloric, nitric, or any other single acid.

Analytical Reactions of Gold.

1. Through a few drops of solution of a chloraurate or of an auric salt (the chloride, $AuCl_3$, is the only convenient auric salt) pass hydrogen sulphide in the cold; a black precipitate of aurous-auric sulphide, Au_2S_2, is produced. This precipitate dissolves, with difficulty, in yellow ammonium sulphide. If the hydrogen sulphide be passed through a boiling solution, a brown precipitate of metallic gold is produced.

2. To a solution of a chloraurate or of a gold salt add a

rrous salt, and set aside; metallic gold is precipitated in e form of a yellowish or reddish-brown lustrous powder, ferric salt remaining in solution. Oxalic acid, also, and ost free metals similarly precipitate gold, the supernatant quid acquiring a purplish hue.

This is a convenient way of preparing pure gold, or *fine* *ld,* as it is termed, or of working up the gold residues from boratory operations. The precipitate, after boiling with ydrochloric acid, washing and drying, may be obtained as button by mixing with an equal weight of borax or acid tassium sulphate and fusing in a crucible in a good furnace.

3. Add a few drops of dilute solutions of stannous and annic chlorides to a considerable quantity of distilled water; our the liquid, a small quantity at a time, into a very dilute lution of auric chloride, and stir well; the mixture assumes purple tint, and flocks of a precipitate, known as the *Purple* *Cassius* (from the name of the discoverer, M. Cassius), are roduced. The presence of more than a trace of free acid ust be avoided.

Purple of Cassius is also formed on immersing a piece of n foil in a solution of auric chloride; it is said to be a ixture of auric, aurous, stannic, and stannous oxides; but cent experiments suggest that it may be merely stannic id, mechanically coloured with metallic gold. It is the louring agent in the finer varieties of ruby glass.

PLATINUM : Pt. Atomic weight, 193·3

Occurrence.—Platinum, like gold, occurs in nature in the ee state, the chief sources of supply being Mexico, Brazil, d Siberia. Alloyed with iridium, osmium, and other rare etals, it is met with in the form of grey grains or powder alluvial deposits, frequently associated with gold. It is parated from the soil by washing.

Uses.—Platinum is chiefly employed in the form of foil, re, crucibles, spatulas, capsules, evaporating-dishes, and lls, for the purposes of the analyst and chemical manufacrer. It is tolerably hard, fusible with very great difficulty, and not dissolved by hydrochloric, nitric, or sulphuric acid; but it is somewhat readily attacked by alkaline substances. It is dissolved by aqua regia with production of chloroplatinic acid, H_2PtCl_6. It forms fusible alloys with lead and other metals, and with phosphorus an easily fused phosphide. None of these substances, therefore, nor mixtures which may yield any of them, should be heated in platinum vessels. Hammered platinum vessels are the most durable. They are best cleaned by fusing a small quantity of acid potassium sulphate in them, and dissolving out the fused salt by boiling in water. They should not be either heated or cooled very suddenly. They should only be heated in the upper portion of the Bunsen or blowpipe-flame, as exposure to the lower parts of these flames, which contain incompletely burnt gases, gives rise to the formation of a brittle carbide. Red-hot platinum vessels should not be permitted to come into contact with any metallic support, unless one made of platinum.

The specific gravity of platinum is 21·5; and that of the allied metal, *iridium*, 22·4.

Experiment.—Place a fragment of platinum in a small quantity of aqua regia, and set the vessel aside in a warm place (in a fume-cupboard), adding more acid from time to time if necessary; a solution of chloroplatinic acid, H_2PtCl_6 (formerly regarded as simply a solution of platinic chloride, $PtCl_4$), results. Evaporate the solution to remove excess of acid, and complete the desiccation over a water-bath. Dissolve the residue in water, and retain the solution for subsequent experiments, and as a reagent for the precipitation of potassium and ammonium salts. Platinum treated in this manner, and the resulting chloroplatinic acid dissolved in water, forms "Solution of Platinic Chloride," B.P.

Analytical Reactions of Platinum.

1. Through a few drops of a solution of a chloroplatinate, or of a platinic salt to which an equal quantity of solution of sodium chloride has been added, pass hydrogen sulphide: a dark-brown precipitate of platinic sulphide, PtS_2, is produced. Filter, wash, and add ammonium hydrosulphide; the precipitate dissolves, with some difficulty.

If sodium chloride be not present in the above reaction, e precipitated sulphide will contain platinous chloride, and y detonate if heated.

2. Add excess of sodium carbonate and some sugar to a lution of a chloroplatinate or of platinic chloride, and boil; black precipitate of metallic platinum is produced.

Platinum black is the name of this precipitate. It possesses a high degree a quality common to many substances, of hich platinum is a notable example — that, namely, of sorbing or *occluding* gases. In its ordinary state, after ll washing and drying, it absorbs from the air and retains ny times its own volume of oxygen. A drop of ether or cohol placed on it is rapidly oxidized, the platinum becom- g hot. This action may be prettily shown by pouring a w drops of ether into a beaker, loosely covering the latter th a card, through which there passes a platinum wire, the wer end of which terminates in a short coil or helix near e surface of the ether: on now warming the helix in a me and then rapidly introducing it into the beaker, it will come red-hot and continue to glow. In this experiment rtial combustion goes on between the ether vapour and e concentrated oxygen of the air, the products of the idation revealing themselves by their odour (chiefly that formaldehyde).

3. To a solution of a chloroplatinate or of platinic chloride d solution of ammonium chloride; a yellow crystalline ecipitate of ammonium chloroplatinate, $(NH_4)_2PtCl_6$, is oduced. When it is slowly formed in dilute solutions, the ecipitate is obtained in minute orange prisms. Collect the ecipitate, dry it, and heat it in a small crucible; it is composed, and metallic platinum, in a finely divided grey te (*spongy platinum*), remains.

Potassium chloride, KCl, gives a similar precipitate of tassium chloroplatinate, K_2PtCl_6. Heat decomposes the tassium salt into $Pt + 2KCl + 2Cl_2$, the chlorine escaping d the potassium chloride remaining with the platinum.

The corresponding sodium compound, Na_2PtCl_6, is soluble water.

In working up the platinum residues from laboratory operations, the mixture should be dried, burnt, boiled successively with hydrochloric acid, water, nitric acid, water, then dissolved in aqua regia, excess of acid being removed by evaporation. Ammonium chloride is then added, the precipitate washed with water, dried, ignited, and the resulting spongy platinum retained or converted into chloroplatinic acid. It is by such processes that the native platinum is treated to free it from the rare metals palladium, rhodium, osmium, ruthenium, and iridium. The spongy platinum is converted into the massive condition by hammering it when hot, or by fusing it in the flame of the oxyhydrogen blowpipe.

Occlusion of gases by spongy platinum.—Spongy platinum has great power of occlusion. A small piece held in a jet of hydrogen which is escaping into the air, causes combination of the hydrogen with the oxygen (of the air) occluded by the platinum. The heat given out by this combination eventually raises the platinum to a red heat and the red-hot platinum kindles the hydrogen jet. Döbereiner's self-lighting lamp was constructed to take advantage of this property—the apparatus being essentially a vessel in which hydrogen was generated by the action of dilute sulphuric acid on zinc, and so arranged that on opening the stopcock a jet of hydrogen impinged on some spongy platinum contained in a small cage.

QUESTIONS AND EXERCISES

Define *tinstone*, *stream-tin*, *block-tin*, *grain-tin*, *tin plate*.—What is the difference between stannic acid and metastannic acid?—State the applications of tin in the arts.—Mention the chief tests for stannous and stannic salts.—Name the best antidote in cases of poisoning by tin solutions.—How is gold dust separated from the earthy matter with which it is naturally associated?—How much pure gold do British coin and jewellers' gold contain?—State the average thickness of gold leaf.—What is the weight of a sovereign?—Explain the term "fineness" as applied to gold.—What effect is produced on gold by hydrochloric, nitric, and nitrohydrochloric acids respectively?—By what reagents may metallic gold be precipitated from solution?—How is "purple of Cassius" prepared?—Whence is platinum obtained?—Why are platinum utensils peculiarly adapted for use in chemical laboratories?—How is chloroplatinic acid prepared?—Name the chief tests for platinum.—What is "platinum black"?—What is meant by *occlusion* of gases?—Describe an experiment illustrating the power of occluding gases, possessed by metallic platinum.—How is "spongy platinum" produced?—By what process may platinum be recovered from residues?

IRECTIONS FOR APPLYING THE REACTIONS DESCRIBED IN THE FOREGOING PARAGRAPHS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF A COMPOUND OF ONE OF THE ELEMENTS ARSENIUM AND ANTIMONY; ALSO OF TIN IN THE FORM OF A STANNIC SALT.[*]

Acidulate the liquid with hydrochloric acid, and pass ydrogen sulphide through it:—

An *orange* precipitate indicates antimony.

A *yellow* precipitate indicates arsenium or a stannic salt. o distinguish between arsenium and stannic salt, test the iginal solution with ammonia and with potassium hydroxide. o precipitates: arsenium indicated. For behaviour of annic salt compare p. 218.

The results may be confirmed by the application of other sts.

RECTIONS FOR APPLYING THE REACTIONS DESCRIBED IN THE FOREGOING PARAGRAPHS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF COMPOUNDS OF BOTH ARSENIUM AND ANTIMONY; ALSO POSSIBLY CONTAINING TIN IN THE FORM OF A STANNIC SALT.

Acidulate a small portion of the liquid with hydrochloric id, and pass hydrogen sulphide through it.

Note 1.—If the hydrogen sulphide precipitate is unmistak- ly orange, antimony may be put down as present, and senium only further sought by the application of Fleitmann's st to the original solution, or to the solution of the sulphides aqua regia[†] freed from sulphur by boiling.

Note 2.—Antimonious sulphide is far less readily soluble than arsenious sulphide in solution of ammonium carbonate. But this fact possesses limited analytical value, since, in the case of mixed sulphides, much antimonious sulphide will prevent a small quantity of arsenious sulphide from being dissolved by the ammonium carbonate, while much arsenious sulphide will carry a small quantity of antimonious sulphide into the solution. When the proportions are, apparently, from the colour of the precipitate, less wide, solution of ammonium carbonate may sometimes be found useful in roughly separating the one sulphide from the other. On filtering and neutralizing the alkaline solution by adding an acid, the yellow arsenious sulphide is reprecipitated. The orange antimonious sulphide, and any stannic sulphide present, will remain on the filter.

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[*] Stannic solutions are rarely met with, but these solutions are alt with here, and in the analytical directions immediately following, cause in the ordinary course of systematic analysis, tin (whether esent originally as stannous or as stannic salt) is eventually preitated as yellow *stannic* sulphide along with arsenium and antimony phides, prior to its separation from arsenium and antimony.

[†] *Aqua Regia* is a mixture of hydrochloric acid and nitric acid. It s so called from its property of dissolving gold, the "king" of metals. ur volumes of hydrochloric acid, three of nitric acid, and twenty-five water, mixed and set aside in a glass-stoppered bottle for a fortght, form *Acidum Nitrohydrochloricum Dilutum*, B.P.

Note 3.—Solution of potassium hydrogen sulphite is said by Wöhler to be a good reagent for separating arsenious and antimonious sulphides, the former being soluble, the latter insoluble in the liquid.

Note 4.—Another reagent for separating arsenious from antimonious and stannic sulphides is *concentrated* hydrochloric acid. As little water as possible must be present. On boiling, antimonious and stannic sulphides dissolve, while arsenious sulphide remains insoluble. The liquid, slightly diluted, filtered, mixed with more water, and again treated with hydrogen sulphide, gives orange antimonious sulphide, mixed with stannic sulphide when tin is present. The presence of arsenium may be confirmed by the application of Fleitmann's test to the original solution.

The two processes now to be described for the detection of arsenium and antimony are rather long, and require much care in their performance; but they are useful, because a small quantity of antimony in presence of much arsenium, or *vice versâ*, may be detected by their means. The method for detecting tin will be described later (p. 228).

Detection of Arsenium and Antimony.

First process.—Generate hydrogen, as for Marsh's test (p. 197), and pass it through a small wash-bottle containing solution of lead acetate, to free it from any trace of hydrogen sulphide, and then through a dilute solution of silver nitrate contained in a test-tube. When the hydrogen apparatus is ı good working order, pour into the generating bottle a ıantity of the original solution to be examined, adding it radually to prevent violent action. After the gas has been ıssing for five or ten minutes, examine the contents of the st-tube; arsenium, if present, will be found in the solution the state of arsenious acid,—

$$AsH_3 + 3H_2O + 6AgNO_3 = H_3AsO_3 + 6HNO_3 + 6Ag;$$

hile antimony, if present, will be found in the black prepitate that has fallen, according to the following equation:

$$SbH_3 + 3AgNO_3 = SbAg_3 + 3HNO_3$$

ıe arsenious radical may be detected in the clear, filtered, pernatant liquid, which still contains much silver nitrate, cautiously neutralizing with a very dilute solution of nmonia, or by adding a few drops of solution of silver nmonio-nitrate, yellow silver arsenite being produced. The ıtimony may be detected by washing the black precipite, boiling it in an open dish with solution of tartaric id, adding hydrochloric acid, filtering and passing hydrogen lphide through the solution, orange antimonious sulphide ing precipitated. (Hofmann.)

Second process.—Obtain the metallic deposit in the middle the delivery-tube as already described under Marsh's test. t on the deposit with hydrogen sulphide gas, and then th hydrochloric acid gas, as detailed in reaction 3 of timony (p. 212). If both arsenium and antimony are esent, the deposit, after the action of hydrogen sulphide, ll be found to be of two colours, the yellow arsenious lphide being usually farther removed from the heated rtion of the tube than the orange antimonious sulphide. oreover, subsequent action of hydrochloric acid gas causes disappearance of the antimonious sulphide, which is nverted into chloride and carried off in the stream of gas.

The chief objection to this process is the liability of the erator mistaking sulphur, deposited from the hydrogen phide by the action of heat, for arsenious sulphide. But the presence or absence of arsenium is easily confirmed by applying Fleitmann's test to the original solution, while the process is most useful for the detection of a small quantity of antimony in the presence of much arsenium. On the whole, Hofmann's method is to be preferred.

Detection of Tin.

During the generation of hydrogen arsenide and antimonide in Marsh's apparatus, any stannic chloride present in the original solution under examination is gradually reduced, with deposition of metallic tin. After the testing for arsenium and antimony is concluded, pour out the contents of the generating bottle into a dish; take out the fragments of zinc, first detaching from them any black powdery or spongy deposit; separate the liquid by filtration and wash the residue (which contains any reduced tin together with impurities derived from the zinc). Boil the residue with a small quantity of dilute hydrochloric acid; filter, if necessary, and test the filtrate for stannous salt by adding mercuric chloride. A white precipitate of mercurous chloride indicates the presence of tin. (Compare p. 248.)

The student may now proceed to the analysis of aqueous solutions of salts of any of the metallic elements hitherto considered. The method followed may be that for the separation of the previous three groups, hydrogen sulphide being first passed through the solution to precipitate arsenium and antimony (also tin, if stannic salt be present). The liquid, after the removal, by filtration, of any hydrogen sulphide precipitate and ebullition to expel hydrogen sulphide, is examined by means of the other group-reagents for metals of the iron, zinc, barium, and magnesium groups and then for alkali metals. (Compare pp. 109, 136, 156, 187.) Three or four solutions at least should be examined before proceeding to the next group of metals—copper, mercury, etc.

COPPER: Cu. Atomic weight, 63·12

Occurrence, etc.—The commonest ore of this metal is *copper pyrites*, a copper and iron sulphide, $CuFeS_2$, occurring in Cornwall; Australia and Russia supply *malachite*, a hydroxycarbonate; much ore is also imported from Spain and from outh America. It is smelted in enormous quantities at wansea, South Wales, a locality peculiarly fitted for the eration on account of its proximity to the coal-fields, and s position as a seaport. By Hollway's economical method smelting copper pyrites and other sulphides, after the lphide is once melted, air is driven, not over, as usual, but rough the mass; the combustion of the sulphur then ecomes self-supporting, and is greatly accelerated.

lchemy.—The alchemists termed this metal *Venus*, perps on account of the beauty of its lustre, and gave it her mbol ♀, a compound hieroglyphic also indicating a mixture gold ⊙, and a certain hypothetical substance called acriony ✠, the corrosive nature of which was symbolized by e points of a Maltese cross. To this day the blue showttle in the shop-window of the pharmacist is occasionally namented by such a symbol, indicating, possibly, that the ue liquid in the vessel is a preparation of copper.

Coinage.—The material of our "copper" coinage is now a onze mixture composed, in 100 parts by weight, of 95 pper, 4 tin, and 1 zinc, the same as in the copper coinage France. One pound avoirdupois (7000 grains, or 453·6 mmes) of this alloy is coined into 48 pence, or 80 halfnce, or 160 farthings.

Metallic Copper is used in preparing *Spiritus Ætheris trosi*, B.P.

Copper forms two sets of salts, which are distinguished as *ric* and *cuprous* salts, and may be regarded as related to oxides, CuO and Cu_2O, respectively. Cupric oxide, or ck copper oxide, CuO, may be prepared by heating fragnts of copper to low redness on a piece of earthenware in open fire. Cuprous iodide, CuI, will be subsequently erred to as a convenient form in which to remove iodine m solution, while the formation of cuprous oxide, Cu_2O, der given circumstances, will come under notice as an inator of the presence of sugar in a liquid.

Cupric Sulphate, $CuSO_4,5H_2O$ (*Cupri Sulphas*, B.P.), *blue iol, blue stone*, or *copper sulphate* is the only copper comund much used in pharmacy. It is a by-product in silverning ($Ag_2SO_4 + Cu = CuSO_4 + 2Ag$). Some is formed in sting copper pyrites. In the latter case, some iron phide and copper sulphide are oxidized to sulphates; but low red heat finally employed decomposes the ferrous sulphate, while the cupric sulphate is unaffected; the latter is purified by crystallization from a hot aqueous solution, though frequently much ferrous sulphate remains in the crystals. Cupric sulphate is also prepared by dissolving in dilute sulphuric acid the black oxide, CuO, obtained in annealing copper plates ($CuO + H_2SO_4 = CuSO_4 + H_2O$); it may also be obtained by boiling copper with three times its weight of sulphuric acid ($2H_2SO_4 + Cu = CuSO_4 + SO_2 + 2H_2O$), diluting, filtering, evaporating, and crystallizing. In this process some black cuprous sulphide also is formed.

Anhydrous Cupric Sulphate, $CuSO_4$, is a yellowish-white powder prepared by depriving the ordinary blue crystals of cupric sulphate of their water of crystallization by exposing them to a temperature of about 400° F. (204° C.). It is used in testing alcohol and similar spirituous liquids for water, becoming blue if the latter be present.

Experiment.—Cupric Nitrate.—Digest copper in dilute nitric acid. When action has ceased, evaporate and crystallize. If the crystals form at a temperature of 73° to 80° F. (22·7 to 26·6° C.), they are prismatic, $Cu(NO_3)_2, 3H_2O$; at lower temperatures, tabular, $Cu(NO_3)_2, 6H_2O$.

$$\underset{\text{Copper}}{3Cu} + \underset{\text{Nitric acid}}{8HNO_3} = \underset{\text{Cupric nitrate}}{3Cu(NO_3)_2} + \underset{\text{Nitric oxide}}{2NO} + \underset{\text{Water}}{4H_2O}$$

Verdigris (from *verdi-gris*, Sp., green-grey) is Copper Oxyacetate (B.P.), $Cu_2O(C_2H_3O_2)_2$, obtained by exposing alternate layers of copper and fermenting refuse grape-husks to the action of air. Digested with twice its weight of acetic acid and a little water, the mixture being evaporated to dryness and the residue dissolved in water, it forms the official Solution of Copper Acetate, $Cu(C_2H_3O_2)_2$.

The modes of forming *Cupric Sulphide, Hydroxide, Oxide, Ferrocyanide*, and *Arsenite*, as well as *Metallic Copper*, are incidentally alluded to in the following analytical paragraphs.

Analytical Reactions of Cupric Salts.

1. Pass hydrogen sulphide through an acidulated solution of a cupric salt; a black precipitate of cupric sulphide, CuS, is produced, which is insoluble in dilute acids.

2. To an aqueous solution of a cupric salt add ammonium

ydrosulphide ; by this reagent, also, cupric sulphide is ecipitated, insoluble in excess.

Note.—Cupric sulphide is not altogether insoluble in mmonium hydrosulphide if free ammonia or much ammonium salt be present ; it is insoluble in potassium and dium hydrosulphides.

3. Immerse a piece of iron or steel, such as the point of penknife or a piece of iron wire, in a few drops of a lution of a cupric salt ; copper is deposited on the iron, ith its characteristic colour, an equivalent quantity of iron ssing into solution. If a sufficient quantity of iron is nployed and the experiment is allowed to continue long ough, the copper is entirely precipitated—

$$CuSO_4 + Fe = FeSO_4 + Cu.$$

 this reaction copper may be recovered on the large scale om waste solutions, old hoop or other scrap iron being rown into the liquors.

4. Add ammonia to a solution of cupric sulphate ; cupric ydroxide, $Cu(OH)_2$, of a light-blue colour, is precipitated. dd excess of ammonia ; the precipitate is redissolved, forming a blue solution of ammonio-cupric salt, so deep in colour to render ammonia an exceedingly delicate reagent for opper. From this ammoniacal solution alcohol precipitates dark-blue crystalline mass ($CuSO_4$, $4NH_3$, H_2O), which, on eating to 150° C., loses water and two molecules of ammonia, ecoming $CuSO_4$, $2NH_3$, and at 200° C. it loses another olecule of ammonia, becoming $CuSO_4$, NH_3. Other soluble pric salts yield similar compounds.

An ammonio-cupric sulphate may be obtained in large ystals by adding saturated solution of ammonia to powdered pric sulphate until the salt is dissolved, placing the liquid a test-glass or cylinder, cautiously pouring in twice its olume of nearly anhydrous alcohol or methylated spirit, aking care that the liquids do not become mixed, tying a piece of bladder over the mouth of the vessel, and setting aside for some weeks in a cool place. (Wittstein.)

5. Add a solution of potassium or sodium hydroxide to a cupric solution; cupric hydroxide, $Cu(OH)_2$, is precipitated, insoluble in excess. Boil the mixture in the test-tube with excess of potassium or sodium hydroxide; the cupric hydroxide is decomposed, losing the elements of water, and becoming converted into black anhydrous cupric oxide, CuO.

6. Add solution of potassium ferrocyanide, K_4FeCy_6, to an aqueous cupric solution; a reddish-brown precipitate of cupric ferrocyanide, Cu_2FeCy_6, is produced. This is an extremely delicate test for copper.

7. Add solution of potassium iodide to an aqueous cupric solution; in moderately concentrated solutions a precipitate of cuprous iodide, CuI, is produced, with simultaneous liberation of iodine which imparts a yellow or brown colour to the solution.

$$2CuSO_4 + 4KI = 2K_2SO_4 + 2CuI + I_2$$

On adding to the mixture a solution of sulphurous acid (or of ferrous sulphate), the colour due to the free iodine is removed, and the nearly white cuprous iodide can be recognised. Even in very dilute cupric solutions a yellow coloration is produced on the addition of potassium iodide, which becomes violet on the addition of starch paste (*see* Iodides, p. 293). This test is even more delicate than the ferrocyanide test, but care must be taken to ascertain that the solution of potassium iodide employed does not contain free iodine.

8. To a cupric solution add solution of arsenious acid, and cautiously neutralize with alkali; green cupric arsenite, $CuHAsO_3$, is produced.

Most copper salts impart a green colour to the Bunsen flame. Cupric chloride imparts a bluish colour.

Antidotes.—In cases of poisoning by compounds of copper, ron filings should be administered, the action of which is explained in reaction 3. Potassium ferrocyanide may also be given (*see* reaction 6). Albumen forms with copper salts a compound insoluble in water, hence raw eggs may be administered, vomiting being induced or the stomach-pump, or stomach-siphon, applied as speedily as possible.

QUESTIONS AND EXERCISES

Name the sources of copper.—What proportion of copper is contained in English and French "copper" coins?—Give equations showing how Cupric Sulphate is prepared on the small and on the large scale.—Calculate how much Crystallized Cupric Sulphate may be obtained from 100 parts of cupric sulphide. *Ans.* 261·05 parts.—How may Cupric Oxide be prepared?—Write down the formula of Verdigris.—What is the analytical position of copper?—Mention the chief tests for copper.—How may copper be separated from arsenium?—Why is finely divided iron an antidote in poisoning by copper?

MERCURY : Hg. Atomic weight, 198·8

Occurrence.—Mercury occurs in nature as sulphide, HgS, forming the ore *cinnabar* (an Indian name expressive of something red), and is obtained from Spain, California, Eastern Hungary, China, Japan, and Peru.

Preparation.—The metal is separated by roasting off the sulphur and then distilling; or better, by distilling with lime, which combines with and retains the sulphur.

Properties.—Mercury (*Hydrargyrum,* B.P.) is a silver-white, lustrous metal, liquid at ordinary temperatures. It boils at 662° F. (350° C.), and at −40° F. (−40° C.) solidifies to a malleable mass of octahedral crystals. Its specific gravity is 13·6. When quite free from other metals, it does not tarnish, and its globules roll freely over a sheet of white paper without leaving any streak.

Formula.—The formula of the mercury molecule is Hg and not Hg_2, because (at all events at the high temperature at which alone the weight of its vapour can be determined) the quantity of mercury vapour which occupies the same space as that occupied by 2 grammes of hydrogen under the same conditions is 198·8 grammes, and not twice this quantity (*see* p. 51). Analogous facts have been observed with reference to the vapours of zinc and cadmium. Mercury, like iron, copper, etc., forms two sets of salts. These are called mercurous and mercuric salts, and correspond to the oxides, Hg_2O and HgO, respectively.

Amalgams.—The mixture or compound formed on fusing metals together is usually termed an *alloy* (*ad* and *ligo,* I bind); but if mercury is a constituent, an *amalgam* (*μάλαγμα, malagma,* from *μαλάσσω, malasso,* I soften, the presence of mercury lowering the melting-point of such a mixture). Most metals form amalgams. *Electric amalgam,* the exciting material which is rubbed against the glass plate of an electrical machine, commonly consists of 1 part each of tin and zinc with 3 parts of mercury. Sodium amalgam has already been mentioned (p. 95).

Medicinal Compounds.—The compounds of mercury used in medicine are all obtained from the metal. The metal itself, rubbed with chalk, or with confection of roses and powdered liquorice-root, or with lard and suet, until globules are not visible *to the unaided eye,* is often used in medicine. The preparations are:—*Hydrargyrum cum Creta,* B.P., or Grey Powder; *Pilula Hydrargyri,* B.P., or Blue Pill (*Massa Hydrargyri,* U.S.P.); and *Unguentum Hydrargyri,* B.P., Mercury Ointment, or Blue Ointment. There are also a Compound Ointment, a Mercurial Plaster, an Ammoniacum and Mercury Plaster, and a Liniment of Mercury, all official. Their therapeutic effects are probably due, not to the large quantity of metallic mercury in them, but to the small quantities of black and red oxide which occur in them through the action of the oxygen of the air on the finely divided metal. The proportion of oxide or oxides varies according to the age of the specimen. All these medicinal preparations of metallic mercury are indefinite and unsatisfactory, and that through no fault of the pharmacist. They much need investigation by pharmacologists and therapeutists.

Mercurous and Mercuric Iodides

Experiment 1.—Rub together small quantities of mercury and iodine, controlling the rapidity of combination by adding, at the outset and at intervals during the operation, a few drops of alcohol, which by evaporation absorbs heat, and thus keeps down the temperature. The product is either mercuric iodide, mercurous iodide, or a mixture of the two, together with mercury or iodine, if excess of either has been employed. If the two elements have been weighed out in atomic proportions, 198·8 of mercury to 125·9 of iodine (about 8 to 5), a green or greyish-green powder results from their union, which consists chiefly of mercurous iodide, HgI; if in the proportion of the atomic weight of mercury to twice that of iodine (198·8 to twice 125·9, or about 4 to 5), red mercuric iodide, HgI_2, results—an iodide that is official, but made in another way (*see* p. 236). Mercurous iodide should be made and dried without heating, and with as little exposure to light as possible. Mercuric iodide may be removed from it by well washing with alcohol. Mercurous iodide can also be obtained as a bright yellow precipitate by adding a solution of potassium iodide to a solution of mercurous nitrate, care being taken that excess of the former is avoided. (*See* reaction 2, p. 247.)

Mercurous iodide is decomposed slowly by exposure to light, and quickly by the action of heat, into mercuric iodide and mercury. Mercuric iodide, occurring as an impurity in mercurous iodide may be detected by digesting in ether (in which mercurous iodide is insoluble), filtering, and evaporating to dryness; mercuric iodide remains. Mercuric iodide is stable, and may be sublimed in scarlet crystals without decomposition. (For the mechanical details of the method by which a specimen of the crystals may be obtained, and the precautions to be observed, *see corrosive sublimate*, p. 239.)

Red and Yellow Varieties of Mercuric Iodide. In condensing, mercuric iodide is at first yellow, afterwards acquiring its characteristic scarlet colour. This may be shown by smearing or rubbing a sheet of white paper with the red iodide, and then holding the sheet before a fire or over a flame for a few seconds. As soon as the paper becomes sufficiently hot the red iodide changes to yellow, and the salt does not quickly regain its red colour when cold if the paper is carefully handled. But if the salt be pressed or rubbed in any way, the portions touched immediately return to the scarlet condition. These colour changes are accompanied by changes in crystalline form. The red modification, stable at ordinary temperatures, forms tetragonal crystals; the yellow modification, rhombic crystals.

Experiment 2.—Preparation of Red or Mercuric Iodide by Precipitation.—To a few drops of a solution of a mercuric salt (corrosive sublimate, for example) add solution of potassium iodide, drop by drop; a precipitate of mercuric iodide forms, and at first redissolves in the excess of the mercuric salt, but is permanent when sufficient iodide has been added. Continue the addition of potassium iodide; the precipitate is redissolved, with formation of potassium mercuric iodide, $KHgI_3$.

$$\underset{\text{Mercuric chloride}}{HgCl_2} + \underset{\text{Potassium iodide}}{2KI} = \underset{\text{Mercuric iodide}}{HgI_2} + \underset{\text{Potassium chloride}}{2KCl}$$

$$\underset{\text{Mercuric iodide}}{HgI_2} + \underset{\text{Potassium iodide}}{KI} = \underset{\text{Potassium mercuric iodide}}{KHgI_3}$$

Notes.—When first precipitated, mercuric iodide is yellowish-red, but soon changes to scarlet.—Its solubility either in solution of the mercuric salt or in solution of potassium iodide renders the detection of a small quantity of a mercuric salt by means of potassium iodide, or a small quantity of an iodide by means of a mercuric solution, difficult, and hence lessens the value of the reaction as a test.—But the reaction is important as the official method for the preparation of mercuric iodide (*Hydrargyri Iodidum Rubrum*, B.P.). Mercuric iodide made in this way has the same composition as that prepared by direct combination of its elements. In making the preparation, the two salts must be used in the proportion of $HgCl_2$ (= 269·18) to 2KI (= 329·46). The mercury in mercuric or mercurous iodide is set free, and sublimes in globules, on heating either powder with dried sodium carbonate in a test-tube; the iodine may be detected by digesting with solution of caustic soda, filtering, and to the solution of sodium iodide thus formed adding starch-paste, acidulating with dilute hydrochloric or sulphuric acid, and adding a solution of a nitrite, when blue starch iodide results.—Mercuric iodide is insoluble in water, slightly soluble in alcohol, tolerably soluble in ether.—Precipitated mercuric iodide mixed with benzoated lard forms *Unguentum Hydrargyri Iodidi Rubri*, B.P.

Mercurous and Mercuric Nitrates

Experiment 3.—Place a globule of mercury, about half the size of a pea, in a test-tube; add twenty or thirty drops of nitric acid; boil slowly until red fumes no longer form; set aside. On cooling, if a globule of mercury still remains in the tube, crystals of mercurous nitrate separate. These may be dissolved in water slightly acidulated with nitric acid. The solution may be retained for subsequent analytical operations.

$$3Hg + 4HNO_3 = 3HgNO_3 + 2H_2O + NO$$

Experiment 4.—Place mercury in *excess* of concentrated nitric acid, and warm the mixture; mercuric nitrate is formed, and will be deposited in crystals as the solution cools. Or, to crystals of mercurous nitrate add nitric acid, and boil until red fumes are no longer evolved. Retain the product for a subsequent experiment.

$$\underset{\text{Mercury}}{3Hg} + \underset{\text{Nitric acid}}{8HNO_3} = \underset{\text{Mercuric nitrate}}{3Hg(NO_3)_2} + \underset{\text{Nitric oxide}}{2NO} + \underset{\text{Water}}{4H_2O}$$

When mercury and nitric acid are boiled together, mercurous nitrate is formed if the mercury be in excess, while mercuric nitrate is produced if the acid be in excess.

Mercuric Oxynitrates.—From the normal mercuric nitrate several oxynitrates may be obtained. Thus on merely evaporating a solution of mercuric nitrate, and cooling, crystals having the formula $Hg_2O(NO_3)_2,2H_2O$ are deposited. The latter, by washing with cold water, yield a *yellow* pulverulent oxynitrate, $Hg_3O_2(NO_3)_2$: mixed with lard, this has sometimes been used as an ointment. By prolonged treatment with water, the yellow oxynitrate eventually yields mercuric oxide.

The official preparations of mercuric nitrate are *Liquor Hydrargyri Nitratis Acidus*, *Unguentum Hydrargyri Nitratis*, and *Unguentum Hydrargyri Nitratis Dilutum*. The *Liquor* is made by placing four ounces of mercury in five fluid ounces of nitric acid diluted with an ounce and a half of water, and when the metal has dissolved, boiling gently for fifteen minutes.

Mercurous and Mercuric Sulphates

Experiment 5.—Boil two or three grains of mercury with a few drops of concentrated sulphuric acid in a test-tube or small dish, in a fume-cupboard; sulphurous anhydride is evolved, and mercuric sulphate, $HgSO_4$, a white, heavy, crystalline powder results.

$$\underset{\text{Mercury}}{Hg} + \underset{\substack{\text{Sulphuric}\\ \text{acid}}}{2H_2SO_4} = \underset{\substack{\text{Mercuric}\\ \text{sulphate}}}{HgSO_4} + \underset{\substack{\text{Sulphurous}\\ \text{anhydride}}}{SO_2} + \underset{\text{Water}}{2H_2O}$$

Between two and three ounces of mercuric sulphate may be prepared from a fluid drachm of mercury and a fluid ounce of sulphuric acid boiled together in a small dish. The operation is completed and any excess of acid removed by cautiously evaporating the mixture of metal and liquid to dryness, in a fume-cupboard (sulphuric acid vapours being excessively irritating to the mucous membrane of the nose and throat); dry crystalline mercuric sulphate remains. If residual particles of mercury are observed, the mass should be moistened with sulphuric acid and again carefully heated.

By-products.—In chemical manufactories, secondary products, such as the sulphurous anhydride of the above reaction, are termed *by-products*, and, if of value, are utilized. In the present case the gas is of no immediate use, and is therefore allowed to escape. When very pure sulphurous anhydride is required for experiments on the small scale, this would be the best method of making it, a delivery-tube being adapted by means of a cork to the mouth of a flask containing the acid and metal.

Mercuric Oxysulphate.—Water decomposes mercuric sulphate into a soluble acid salt and an insoluble yellow oxysulphate, $Hg_3O_2SO_4$. The latter is called *Turpeth mineral*, from its resemblance in colour to *vegetable turpeth*, the powdered root of *Ipomæa turpethum*, an Indian substitute for jalap. It is included in the U.S.P. (*Hydrargyri Subsulphas Flavus*), and was formerly official in Great Britain.

Experiment 6.—Rub a portion of the dry mercuric sulphate of the preceding experiment with as much mercury as it already contains; the product, when the two have completely combined, is mercurous sulphate, Hg_2SO_4: it may be retained for a subsequent experiment. The exact proportion of mercury to mercuric sulphate is merely a matter of calculation based upon the equation representing the chemical change which takes place.

$$HgSO_4 + Hg = Hg_2SO_4$$

Mercurous and Mercuric Chlorides

Experiment 7.—Mix thoroughly a few grains of dry mercuric sulphate with about four-fifths of its weight of sodium chloride, and heat the mixture, slowly, in a test-tube in a fume-cupboard; mercuric chloride, $HgCl_2$, or corrosive sublimate, bichloride or perchloride of mercury (*Hydrargyri Perchloridum*, B.P.), sublimes and condenses in the upper part of the tube in heavy colourless crystals.

Somewhat larger quantities (in the proportion of 20 of mercuric sulphate to 16 of sodium chloride and, *vide infra*, 1 of black manganese oxide) may be sublimed in a pair of two-ounce or three-ounce round-bottomed gallipots, the one inverted over the other, and the joint luted by means of moist fireclay (the powdered clay kneaded with water to the consistence of dough). The luting having been allowed to dry (somewhat slowly to avoid cracks), the pots are placed upright on a sand-bath, sand piled round the lower and a portion of the upper pot, and the whole heated over the flame of a good Bunsen burner for an hour or more in a fume-cupboard (*see* fig. 36—in which the pots are represented as raised in order to show the joint). Mercuric iodide, and calomel, may be sublimed in the same way. The temperature required for the former is somewhat lower than that for corrosive sublimate while that for the latter is higher.

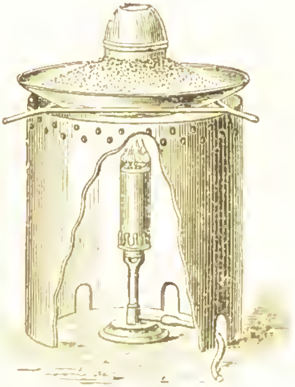

Fig. 36.—Sublimation.

$$\underset{\substack{\text{Mercuric}\\\text{sulphate}}}{HgSO_4} + \underset{\substack{\text{Sodium}\\\text{chloride}}}{2NaCl} = \underset{\substack{\text{Mercuric}\\\text{chloride}}}{HgCl_2} + \underset{\substack{\text{Sodium}\\\text{sulphate}}}{Na_2SO_4}$$

Note.—If the mercuric sulphate contain any mercurous sulphate, some calomel may be formed. This result will be avoided if 2 or 3 per cent. of black manganese oxide be previously mixed with the ingredients. The action of this oxide is to turn out from the excess of sodium chloride used in the process the chlorine necessary to convert any calomel into corrosive sublimate, sodium manganate and a lower manganese oxide being simultaneously produced.

Precaution.—The operation must be conducted with care in a fume-cupboard, because the vapour of corrosive sublimate, which might possibly escape, is very acrid and highly poisonous. Mercuric chloride volatilizes, though extremely slowly and slightly, at the ordinary temperature of warm weather.

A solution of ten grains of mercuric chloride in one pint of water forms *Liquor Hydrargyri Perchloridi*, B.P. Unless preserved in an amber-coloured bottle, a very dilute aqueous solution of mercuric chloride, when long kept, is liable to decomposition, calomel being precipitated, water decomposed, hydrochloric acid formed, and oxygen evolved.

Experiment 8.—Mix a few grains of the mercurous sulphate from experiment 6 with about a third of its weight of sodium chloride, and sublime in a test-tube; crystalline mercurous chloride, HgCl, or calomel (*Hydrargyri Subchloridum*, B.P.) results. Larger quantities may be prepared in the manner directed for corrosive sublimate, a somewhat higher temperature being employed: similar precautions must also be observed.

$$\underset{\substack{\text{Mercurous}\\ \text{sulphate}}}{Hg_2SO_4} + \underset{\substack{\text{Sodium}\\ \text{chloride}}}{2NaCl} = \underset{\substack{\text{Mercurous}\\ \text{chloride}}}{2HgCl} + \underset{\substack{\text{Sodium}\\ \text{sulphate}}}{Na_2SO_4}$$

Calomel may also be made by other methods. The name *calomel* (καλὸς, *kalos*, good, and μέλας, *melas*, black) was probably indicative of the esteem in which black mercuric sulphide (the compound to which the name calomel was first applied) was held.

Test for corrosive sublimate in calomel.—If the mercurous sulphate employed in this experiment contain mercuric sulphate, some mercuric chloride will also be formed. Corrosive sublimate is soluble in water, calomel insoluble; the presence of the former may therefore be proved by boiling a few grains of the calomel in distilled water, filtering and testing by means of hydrogen sulphide or ammonium hydrosulphide as described hereafter. Or two or three grains of the suspected calomel may be mixed with a drop of 10 per cent. alcoholic soap solution and a drop of freshly prepared alcoholic solution of guaiacum resin, and the mixture well stirred with 2 c.c. of ether. On evaporating the ethereal solution, the presence of mercuric chloride is indicated by an intense green coloration. If corrosive sublimate be present, the whole bulk of the calomel must be washed with hot distilled water till the filtrate ceases to give any indications of the impurity. Corrosive sublimate is more soluble in alcohol, and still more in ether, than it is in water, while calomel is insoluble in all three. Ether in which calomel has been digested should therefore, after filtration, yield no residue on evaporation. Calomel is converted by hydrocyanic acid into mercuric cyanide and a black powder readily yielding metallic mercury. Powell and Bayne have shown that a certain proportion of hydrochloric acid arrests this action.

Calomel mixed with benzoated lard forms *Unguentum Hydrargyri Subchloridi*, B.P., and with sulphurated antimony, guaiacum resin, and castor-oil, it forms *Pilula Hydrargyri Subchloridi Composita*, B.P., or Plummer's Pill.

Note.—Carefully purified cotton, bleached by dilute bleaching-powder solution and thoroughly washed, takes up mercury from dilute solutions of mercuric chloride, leaving the solution relatively richer in chlorine; part of the mercury so taken up exists as unchanged mercuric chloride, part as mercurous chloride, and part as mercuric oxide. Hence, solutions of mercuric chloride should not be filtered through cotton wool.

Mercuric Oxide

Experiment 9.—Evaporate to dryness, in a small dish in a fume-cupboard, the mercuric nitrate from experiment 3, and heat the residue till no more nitrous fumes are evolved; red mercuric oxide, HgO, *red precipitate* (*Hydrargyri Oxidum Rubrum*, B.P.) remains.

$$\underset{\text{Mercuric nitrate}}{2Hg(NO_3)_2} = \underset{\text{Mercuric oxide}}{2HgO} + \underset{\text{Nitrogen peroxide}}{4NO_2} + \underset{\text{Oxygen}}{O_2}$$

A much larger yield of mercuric oxide (for the same quantity of nitric acid used to dissolve mercury) may be obtained by heating mercurous nitrate, or by thoroughly mixing with the dry mercuric nitrate from experiment 4 (prior to heating it) as much mercury as it already contains (ascertained by calculation from the atomic weights and the weight of mercuric nitrate employed, as in making mercurous sulphate). In this case the free mercury is also converted into mercuric oxide.

$$\underset{\text{Mercuric nitrate}}{Hg(NO_3)_2} + \underset{\text{Mercury}}{Hg} = \underset{\text{Mercuric oxide}}{2HgO} + \underset{\text{Nitrogen peroxide}}{2NO_2}$$

Mercuric oxide is tested for nitrate by heating a little of the sample in a test-tube, when orange nitrous vapours are produced and are visible in the upper part of the tube, if nitrate be present.

Mercuric oxide is an orange-red or red powder, more or less crystalline according to the extent to which it may have been stirred during preparation from the nitrate. Mixed with hard and soft paraffins, it forms *Unguentum Hydrargyri Oxidi Rubri,* B.P. (1 part in 10). Mercuric oxide, in contact with oxidizable organic matter, is liable to reduction to black or mercurous oxide.

The earliest mode of preparing mercuric oxide consisted in maintaining mercury at a temperature near its boiling-point for many days in vessels, nearly closed to the air, in which a large surface of the metal was exposed. A red powder, which was called *precipitatum per se,* was gradually formed. It was from mercuric oxide so prepared that Priestley first obtained oxygen.

Experiment 10.—To solution of caustic potash or caustic soda, or to lime-water, in a test-tube or larger vessel, add solution of corrosive sublimate, mercuric nitrate, or almost any other mercuric salt (but not mercuric cyanide); yellow mercuric oxide, HgO (*Hydrargyri Oxidum Flavum,* B.P.), is precipitated.

$$\underset{\substack{\text{Mercuric}\\\text{chloride}}}{HgCl_2} + \underset{\substack{\text{Calcium}\\\text{hydroxide}}}{Ca(OH)_2} = \underset{\substack{\text{Mercuric}\\\text{oxide}}}{HgO} + \underset{\substack{\text{Calcium}\\\text{chloride}}}{CaCl_2} + \underset{\text{Water}}{H_2O}$$

Twenty grains of corrosive sublimate to ten ounces of solution of lime forms *Lotio Hydrargyri Flava,* B.P. The precipitate only differs physically from red mercuric oxide; the yellow oxide is more minutely divided than the red. Mixed with soft paraffin, it forms *Unguentum Hydrargyri Oxidi Flavi*, B.P. (1 part in 50).

Mercurous Oxide

Experiment 11.—To calomel add solution of caustic potash or caustic soda, or lime-water; black mercurous oxide, Hg_2O, is produced, and may be filtered off, washed and dried. This reaction, and the formation of a white curdy precipitate on the addition of solution of silver nitrate to the filtrate from the mercurous oxide, acidulated by nitric acid, form sufficient evidence that a powder consists of or contains calomel. The curdy precipitate is silver chloride.

Thirty grains of mercurous chloride, triturated with $\frac{1}{2}$ fluid ounce of glycerin, and $1\frac{1}{4}$ fluid ounce of mucilage of tragacanth, and the quantity made up to 10 fluid ounces with solution of lime, form black wash (*Lotio Hydrargyri Nigra*, B.P.).

$$\underset{\substack{\text{Mercurous}\\\text{chloride}}}{2HgCl} + \underset{\substack{\text{Calcium}\\\text{hydroxide}}}{Ca(OH)_2} = \underset{\substack{\text{Mercurous}\\\text{oxide}}}{Hg_2O} + \underset{\substack{\text{Calcium}\\\text{chloride}}}{CaCl_2} + \underset{\text{Water}}{H_2O}$$

Analytical Reactions of Mercury Compounds.

The Copper Test (for Mercurous or Mercuric Salts).—Place a small piece of bright copper, about half an inch long and a quarter of an inch broad, in a solution of any salt of mercury, mercurous or mercuric, and heat in a test-tube; the copper becomes coated with mercury in a fine state of division. (The absence of any notable quantity of nitric acid must be ensured, or the whole of the copper will be dissolved. *See* p. 244.) Pour away the supernatant liquid from the copper, wash the latter in the tube once or twice with water, remove the metal, dry it by gentle pressure in a piece of filter-paper, place it in a dry, narrow test-tube, and heat to redness in a Bunsen flame, the tube being held in an almost horizontal position; the mercury volatilizes and condenses as a whitish sublimate of minute globules on the cool part of the tube. The globules aggregate on being gently pressed with a glass rod, and are especially visible where flattened between the rod and the side of the test-tube.

Notes on the Test.—This is a valuable test for several reasons:—It is very delicate when performed with care. It separates from the substance under examination, mercury itself, an element which, from its metallic lustre and fluidity, cannot be mistaken for any other. It is applicable to both mercurous and mercuric salts. It renders possible the detection of mercury in the presence of most other substances, organic or inorganic.

In performing the test, the presence of any considerable quantity of nitric acid may be avoided by adding an alkali until a slight permanent precipitate appears, and then very slightly reacidifying with a drop or two of acetic acid; or by concentrating in an evaporating-dish after adding a little sulphuric acid and then rediluting.

Analytical Reactions of Mercuric Salts.

1. To a few drops of a solution of a mercuric salt (corrosive sublimate, for example) add solution of potassium iodide, drop by drop; a yellowish-red precipitate of mercuric iodide, HgI_2, forms, and at first redissolves, but is permanent when sufficient potassium iodide has been added. Continue the addition of potassium iodide; the precipitate is redissolved. (*See Notes* on p. 236.)

Ammoniated Mercury

2. Add a solution of a mercuric salt to solution of ammonia, taking care that the mixture, after well stirring, still smells of ammonia; a white precipitate is produced.

Performed in a test-tube, this reaction is a very delicate test for the presence of a mercuric salt; performed in larger vessels, the mercuric salt being corrosive sublimate (3 ounces dissolved in 3 pints of distilled water, the solution poured into 4 fluid ounces of Solution of Ammonia, and the precipitate washed and then dried on a water-bath), it is the process for the preparation of *white precipitate*, formerly called ammonio-chloride of mercury, now known as Ammoniated Mercury (*Hydrargyrum Ammoniatum*, B.P.).

$$\underset{\substack{\text{Mercuric}\\ \text{chloride}}}{HgCl_2} + \underset{\text{Ammonia}}{2NH_3} = \underset{\substack{\text{White}\\ \text{precipitate}}}{NH_2HgCl} + \underset{\substack{\text{Ammonium}\\ \text{chloride}}}{NH_4Cl}$$

This precipitate is considered to be mercuri-ammonium chloride, NH_2HgCl,—that is, ammonium chloride, NH_4Cl, in which two atoms of hydrogen are replaced by one atom of mercury. When warmed with caustic potash it evolves ammonia.

Varieties of Ammoniated Mercury.—If the order of mixing the solutions in reaction 2 be reversed, and ammonia be added to solution of mercuric chloride, a double mercuri-ammonium and mercuric chloride, $NH_2HgCl,HgCl_2$, is produced: it contains 76·59 per cent. of mercury. Prior to the year 1826, white precipitate was officially made by adding caustic potash or caustic soda to a solution of equal parts of corrosive sublimate and sal-ammoniac; this gave a double mercuri-ammonium and ammonium chloride, NH_2HgCl,NH_4Cl, containing 65·59 per cent. of mercury. This compound is now known as "*fusible* white precipitate," because at a temperature somewhat below redness it fuses and then volatilizes. The white precipitate, which has been official since 1826, contains, theoretically, 79·54 per cent. of mercury. An ointment prepared with this compound is official (*Unguentum Hydrargyri Ammoniati*, B.P.). Prolonged washing with water converts white precipitate into a yellowish compound (NH_2HgCl, HgO); hence the official preparation is not thoroughly freed from the ammonium chloride which is formed during its manufacture, but which, if present in larger proportion than 7 or 8 per cent., gives to it the character of partial or complete fusibility. The officially recognised ammoniated mercury should volatilize at a temperature below redness without fusing, and should yield 78 to 79 per cent. of metallic mercury. With iodine, chlorine, or bromine, white precipitate may yield the dangerously explosive nitrogen iodide, chloride, or bromide.

Dimercuri-ammonium iodide, NHg_2I, is formed in testing for ammonia by means of Nessler's reagent (which see).

3. Pass hydrogen sulphide through a mercuric solution

until the liquid smells strongly of the gas; a black precipitate of mercuric sulphide, HgS, is produced.

$$\underset{\text{Mercuric chloride}}{HgCl_2} + \underset{\text{Hydrogen sulphide}}{H_2S} = \underset{\text{Hydrochloric acid}}{2HCl} + \underset{\text{Mercuric sulphide}}{HgS}$$

Mercuric sulphide does not dissolve in dilute acids or in ammonium hydrosulphide. In the case of mercuric chloride (or of other mercuric salt to which hydrochloric acid has been added previously), hydrogen sulphide, when added in small quantity, produces a white precipitate. On the addition of more of the reagent, the colour of the precipitate changes through various shades of yellow, orange, and brown, to black. The same white substance may also be obtained by heating a small quantity of black mercuric sulphide with solution of mercuric chloride. Its composition is represented by the formula, $HgCl_2, 2HgS$. The yellow, orange, and brown substances are intermediate in composition between this and mercuric sulphide.

Note.—Hydrogen sulphide also yields a black precipitate with solutions of mercurous salts. In the case of these salts, the precipitate consists of a mixture of mercuric sulphide and mercury (not of mercurous sulphide); hence this reagent does not distinguish between mercurous and mercuric salts. But in the course of systematic analysis, mercuric salts are precipitated from their solutions, as sulphide, after mercurous salts have been removed as chloride.

Red Mercuric Sulphide.—Prolonged contact with hydrogen sulphide or a hydrosulphide, especially if warm, converts the black into a red sulphide. *Vermilion* is mercuric sulphide prepared by sublimation.

Ethiop's Mineral, formerly known as *Hydrargyri Sulphuretum cum Sulphure,* is a mixture of mercuric sulphide and sulphur, obtained by triturating the elements in a mortar till globules of mercury are no longer visible. Its name is probably in allusion to its colour.

Analytical Reactions of Mercurous Salts.

1. To a solution of a mercurous salt (the mercurous nitrate obtained in experiment 2, for example) add hydrochloric acid or other soluble chloride; a white precipitate of mercurous chloride, calomel, HgCl, is produced.

2. To a solution of a mercurous salt add a few drops of a very dilute solution of potassium iodide; a yellow precipitate of mercurous iodide, HgI, is produced.

$$\underset{\substack{\text{Mercurous}\\ \text{nitrate}}}{HgNO_3} + \underset{\substack{\text{Potassium}\\ \text{iodide}}}{KI} = \underset{\substack{\text{Potassium}\\ \text{nitrate}}}{KNO_3} + \underset{\substack{\text{Mercurous}\\ \text{iodide}}}{HgI}$$

Unless very dilute solution of potassium iodide is employed, it is difficult to obtain a pure yellow precipitate, a greenish mixture of mercurous iodide and mercury being generally formed, owing to the decomposition of some of the former by excess of potassium iodide; a considerable excess completely decomposes the mercurous iodide, forming potassium mercuric iodide and mercury.

$$2HgI + KI = KHgI_3 + Hg$$

The potassium mercuric iodide is soluble in water, and forms a nearly colourless solution, while the metallic mercury remains as a black precipitate.

3. To a mercurous salt, dissolved or undissolved (*e.g.*, calomel), add ammonia; a black mercuros-ammonium salt (*e.g.*, chloride, NH_2Hg_2Cl), is formed. It seems probable that the so-called mercuros-ammonium salts are really mixtures of the mercuri-ammonium compounds (*see* p. 245) with metallic mercury.

Other Tests for Mercury Compounds.

The elimination of mercury in the actual state of metal by the copper test, coupled with the production or non-production of a white precipitate on the addition of hydrochloric acid to the original solution, is usually sufficient evidence of the presence of mercury and of its existence as a mercurous or a mercuric salt. But other tests may sometimes be applied with advantage. Thus metallic mercury is deposited on placing a drop of the solution on a plate of gold (sovereign or half-sovereign), and touching the drop and the edge of the plate simultaneously with a key: an electric current passes, under these circumstances, from the gold to the key, and thence through the liquid to the gold, decomposing the salt, the mercury of which forms a white metallic spot on the gold. This is called the *galvanic test,* and is useful for clinical purposes.——Solution of stannous chloride, $SnCl_2$, from the readiness with which it forms stannic chloride, $SnCl_4$, gives with mercuric solutions a white precipitate of mercurous chloride, and rapidly reduces this mercurous chloride still further to a greyish mass of finely divided mercury; this is the *magpie test,* probably so called from the white and grey appearance of the precipitate. The reaction may also be obtained from even such insoluble mercury compounds as white precipitate.——A confirmatory test for mercuric and mercurous salts will be found in the action of solution of potassium, sodium, or calcium hydroxide. (*See* pp. 242, 243.)——Potassium chromate, K_2CrO_4, gives with mercurous salts, a red precipitate of mercurous chromate, Hg_2CrO_4.——Mercury and all its compounds are more or less completely volatilized when heated in a dry tube, many of the latter being decomposed and yielding globules of metallic mercury.——All dry compounds of mercury are decomposed when heated in a dry test-tube with dried sodium carbonate, mercury subliming and condensing in visible globules, or as a whitish deposit which yields globules when rubbed with a glass rod.

Antidote.—Albumen gives a white precipitate with solutions of mercuric salts; hence the importance of administering white of egg, while waiting for a stomach-pump or stomach-siphon, in case of poisoning by corrosive sublimate.

QUESTIONS AND EXERCISES

Name the chief ore of mercury, and describe a process for the extraction of the metal.—Give the properties of mercury.—In what state does mercury exist in "Grey Powder"?—What other preparations of metallic mercury itself are employed in medicine?—State the relation of the mercurous to the mercuric compounds.—Distinguish between an *alloy* and an *amalgam.*—State the formulæ of the two mercury iodides.—Under what circumstances has mercuric iodide different colours?—Illustrate the chemical law of Multiple Proportions as explained by the atomic theory, employing for that purpose the stated composition of the two mercury iodides.—Write down the formulæ of Mercurous and Mercuric Nitrates and Sulphates.

—How is Mercuric Sulphate prepared?—What is the formula of "Turpeth Mineral"?—Describe the processes necessary for the conversion of mercury into Calomel and Corrosive Sublimate, using equations.—Why is black manganese oxide sometimes mixed with the other ingredients in the preparation of corrosive sublimate?—Give the chemical and physical points of difference between calomel and corrosive sublimate.—How may calomel in corrosive sublimate be detected?—Calculate how much Mercury will be required in the manufacture of one ton of Calomel. *Ans.* 17 cwt. nearly.—Mention the official preparations of the Mercury Chlorides.—Give the formulæ and mode of formation of the Red, Yellow, and Black Mercury Oxides, employing diagrams.—Explain the action of the chief general test for Mercury.—How are mercurous and mercuric salts analytically distinguished?—Give a probable view of the constitution of *Hydrargyrum Ammoniatum*, B.P., and an equation showing how it is made.—State the best temporary antidote to poisoning by mercury.

LEAD : Pb. Atomic weight, 205·35

Occurrence.—The ores of lead are numerous; but the one from which the metal is chiefly obtained is lead sulphide, PbS, *galena* (from γαλήνη, *galēnē*, tranquillity, perhaps from its supposed effect in allaying pain).

Preparation.—The ore is first roasted in a current of air; much sulphur is thus burnt off as sulphurous anhydride, while some of the metal is converted into oxide; a portion of the sulphide is at the same time oxidized to sulphate. Oxidation is then stopped and the temperature raised, whereupon the oxide and sulphate, interacting with undecomposed sulphide, yield the metal and sulphurous anhydride:—$2PbO + PbS = 3Pb + SO_2$; and $PbSO_4 + PbS = 2Pb + 2SO_2$.

Uses.—The uses of lead for making pipes and lead sheeting are well known. Alloyed with some arsenium, it is used in making ordinary *shot*; with tin it forms *solder*; with antimony and tin, *type-metal*; and in smaller quantities it enters into the composition of *Britannia metal*, *pewter*, and other alloys. Lead is so slightly attacked by many dilute acids that chemical vessels and instruments are sometimes made of it. Hot hydrochloric acid slowly converts it into lead chloride with evolution of hydrogen. Cold sulphuric acid in presence of air only very slightly attacks it with formation of lead sulphate and water; hot concentrated sulphuric acid attacks it rapidly with formation of lead sulphate and evolution of sulphurous anhydride. Hot nitric acid converts it into lead nitrate with evolution of nitric oxide.

The lead salts used in pharmacy and all other lead preparations are obtained, directly or indirectly, from the metal itself. Heated to a high temperature in a current of air, lead combines with oxygen and forms lead oxide, PbO, a yellow powder (*massicot*), or, if fused and solidified, a brighter, reddish-yellow, heavy mass of bright scales (*Plumbi Oxidum*, B.P.), termed *litharge* (from λίθος, *lithos*, a stone, and ἄργυρος, *arguros*, silver). It is from this oxide that the chief lead compounds are obtained. Lead oxide, by further heating in a current of air, at a temperature considerably below that at which it was produced, yields *red lead* or *minium*, Pb_3O_4. The latter oxide is intermediate in composition between lead oxide, PbO, and lead peroxide, PbO_2; and, although it is usually represented by the formula Pb_3O_4, it is subject to some variation in composition. Both litharge and red lead are much used by painters, paper-stainers, and glass-manufacturers. *White lead* is lead hydroxycarbonate, $2PbCO_3, Pb(OH)_2$; it is made by exposing lead, cast in spirals or little gratings, to the action of air, acetic acid fumes, and carbonic anhydride, the latter generated from decaying vegetable matter, such as spent tan: lead oxyacetate slowly but continuously forms, and is as continuously decomposed by the carbonic anhydride, with production of hydroxycarbonate, or *dry white lead*. The grating-like masses, when ground, form the heavy, white, pulverulent, official *Plumbi Carbonas*, B.P. The latter is the active constituent of *Unguentum Plumbi Carbonatis*, B.P., formerly known as *Unguentum Cerussæ*. Lead hydroxycarbonate is also made by bringing carbonic anhydride and litharge together in a solution of lead acetate. Ground up with about 7 per cent. of linseed-oil, it forms the *white lead* used by painters and plumbers.

Lead compounds are poisonous, producing saturnine colic, and even paralysis. These effects are termed *saturnine* from an old name of lead, *Saturn*. The alchemists called lead Saturn, first, because they thought it the oldest of the seven then known metals, and it might therefore be compared to Saturn, who was regarded as the father of the gods; and, secondly, because its power of dissolving other metals recalled a peculiarity of Saturn, who was said to be in the habit of devouring his own children.

Lead Acetate

Experiment 1.—Place a few grains of lead oxide in a testube, add about an equal weight of water and two and a half imes its weight of acetic acid, and boil; the oxide dissolves nd forms a solution of lead acetate, $Pb(C_2H_3O_2)_2$. When old, or on evaporation if much water has been used (the olution being kept faintly acid), crystals of lead acetate *Plumbi Acetas*, B.P.), $Pb(C_2H_3O_2)_2, 3H_2O$, are deposited. Larger quantities are obtained by the same method.

$$\underset{\text{Lead oxide}}{PbO} + \underset{\text{Acetic acid}}{2HC_2H_3O_2} = \underset{\text{Lead acetate}}{Pb(C_2H_3O_2)_2} + \underset{\text{Water}}{H_2O}$$

The salt is termed *Sugar of Lead*, from its sweet taste. Besides its direct use in pharmacy it forms rather more than hree-fourths of *Pilula Plumbi cum Opio*, B.P., is the active onstituent of *Unguentum Plumbi Acetatis*, B.P., and an ingredient in *Suppositoria Plumbi Composita*, B.P.

Lead Subacetate or Oxyacetate

Experiment 2.—Boil lead acetate with four times its weight of water and rather more than two-thirds of its weight of lead oxide; the filtered liquor is solution of lead subacetate, *Liquor Plumbi Subacetatis Fortis*, B.P., Goulard's Extract.

The official *Liquor* is made by boiling 5 ounces of acetate and 3½ of oxide in one pint of distilled water for half an hour constantly stirring), filtering, and making up for any loss due to evaporation by diluting the filtrate to 1 pint. It contains about 24 per cent. of lead subacetate, $Pb_2O(C_2H_3O_2)_2$. A similar solution was used by M. Goulard, who drew attention to it in 1770 and called it *Extractum Saturni*. A more dilute solution, 1 of *Liquor* and 1 of 90 per cent. alcohol in 78 of distilled water, is also official in the British Pharmacopœia, under the name of *Liquor Plumbi Subacetatis Dilutus*. The latter is commonly known as *Goulard Water*. A concentrated solution of lead subacetate in glycerin constitutes *Glycerinum Plumbi Subacetatis*, B.P., and this with a mixture of soft and hard paraffins gives *Unguentum Glycerini Plumbi Subacetatis*, B.P., a modification of the original *Goulard's Cerate*.

Lead Nitrate

Experiment 3.—Digest a few grains of red lead in dilute nitric acid; lead nitrate, $Pb(NO_3)_2$, is formed, and remains in solution, while lead peroxide, PbO_2, remains behind as a dark brownish-purple powder. *Lead Nitrate* may be made more directly by dissolving litharge, PbO, in nitric acid. $PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O$.

Lead nitrate or acetate is used officially in preparing lead iodide. For this purpose the above mixture may be filtered, the lead peroxide washed with hot water, the filtrate and washings evaporated to dryness to remove excess of nitric acid, the residual lead nitrate redissolved by boiling with a small quantity of hot water, and the solution set aside to crystallize; or a portion may at once be used for the next experiment. Lead nitrate forms white crystals derived from octahedra.

Lead peroxide, PbO_2, when heated with concentrated hydrochloric acid yields lead chloride, $PbCl_2$, chlorine, and water. $PbO_2 + 4HCl = PbCl_2 + Cl_2 + 2H_2O$.

Lead Iodide

Experiment 4.—To a neutral solution of lead nitrate add solution of potassium iodide; a precipitate of lead iodide, PbI_2 (*Plumbi Iodidum,* B.P.), is produced. Equal weights of the salts may be used in making large quantities.

$$\underset{\text{Lead nitrate}}{Pb(NO_3)_2} + \underset{\text{Potassium iodide}}{2KI} = \underset{\text{Lead iodide}}{PbI_2} + \underset{\text{Potassium nitrate}}{2KNO_3}$$

Heat the lead iodide with the supernatant liquid, and filter if necessary; the salt dissolves, and separates again in golden crystalline scales as the solution cools.

Lead iodide is the active ingredient in *Emplastrum Plumbi Iodidi,* B.P., and *Unguentum Plumbi Iodidi,* B.P. Lead iodide is soluble in solution of ammonium chloride.

Lead Oleate. Lead Plaster

Experiment 5.—Boil together in a small porcelain dish a few grains of very finely powdered lead oxide, with twice its weight of olive-oil, and two or three times its weight of water, well stirring the mixture, and from time to time replacing water that has evaporated; the product is a white mass of lead oleate, $Pb(C_{18}H_{33}O_2)_2$, (*Emplastrum Plumbi,* B.P.), glycerin remaining in solution. Larger quantities are prepared in the same manner.

$$\underset{\text{Lead oxide}}{3PbO} + \underset{\text{Water}}{3H_2O} + \underset{\text{Glyceryl oleate (olive-oil or oleine)}}{2C_3H_5(C_{18}H_{33}O_2)_3}$$

$$= \underset{\text{Lead oleate (lead plaster)}}{3Pb(C_{18}H_{33}O_2)_2} + \underset{\text{Glyceryl hydroxide (glycerin)}}{2C_3H_5(OH)_3}$$

The action between the lead oxide and olive-oil is slow, requiring several hours for its completion.

The *glycerin* may be obtained by treating the aqueous product of the above reaction with hydrogen sulphide to remove a trace of lead, then digesting with animal charcoal, filtering, and evaporating. But on the large scale glycerin is produced as a by-product in the manufacture of soap and candles, since glyceryl compounds are the main constituents of nearly all vegetable and animal fats, and undergo decomposition analogous to that represented above in the course of the manufactures referred to. If in making lead plaster the mixture be evaporated to dryness, some of the glycerin escapes with the steam while some remains with the plaster.

Modes of formation of *Chloride, Sulphide, Chromate, Sulphate, Hydroxide,* and other lead compounds are incidentally described in the following analytical paragraphs.

Analytical Reactions of Lead Salts.

1. To a solution of a lead salt (acetate, for example) add hydrochloric acid; a white precipitate of lead chloride, $PbCl_2$, is obtained. Boil the precipitate with a moderate quantity of water; it dissolves, but is redeposited in small acicular crystals when the solution cools. Filter the cold solution, and pass hydrogen sulphide through it; the formation of a black precipitate of lead sulphide, PbS, shows that the lead chloride is soluble to a slight extent in cold water.

Note.—The formation of a white precipitate (soluble in hot water and blackened by hydrogen sulphide) on the addition of hydrochloric acid, sufficiently distinguishes lead salts from those of other metals; but the non-production of such a precipitate does not prove the absence of a small quantity of lead since lead chloride is slightly soluble in cold water.

2. Through a dilute solution of a lead salt, acidulated with

hydrochloric acid, pass hydrogen sulphide ; a black precipitate of lead sulphide, PbS, is produced.

Lead in Water.—The foregoing is a very delicate test. Should a trace of lead be present in water used for drinking purposes, it may be detected by means of hydrogen sulphide. On passing the gas through a pint of such (acidulated) water, a brownish colour is produced. If the tint is scarcely perceptible, set the liquid aside for a day; the hydrogen sulphide will undergo oxidation and a thin layer of sulphur will be found at the bottom of the vessel, white if no lead sulphide be present in it, but more or less brown if it contain lead sulphide. Hygienists regard one-twentieth of a grain of lead per gallon as dangerous, while a smaller quantity may do harm. Water commonly used for drinking purposes should not contain a trace.

3. To a solution of a lead salt add ammonium hydrosulphide; a black precipitate of lead sulphide, insoluble in excess, is produced.

4. To a solution of a lead salt add solution of potassium chromate, K_2CrO_4 ; a yellow precipitate of lead chromate, $PbCrO_4$, is formed, insoluble in dilute acids and in solution of ammonium chloride.

Chromes.—This reaction has technical as well as analytical interest. The precipitate is the common pigment termed *chrome yellow*, or *lemon chrome.* Boiled with slaked lime and water, a portion of the chromium is removed, together with oxygen, and forms soluble calcium chromate, while lead oxychromate, of a bright orange-red colour (*chrome orange*) is also produced. $2PbCrO_4 + Ca(OH)_2 = CaCrO_4 + Pb_2OCrO_4 + H_2O$.

5. To a solution of a lead salt add dilute sulphuric acid, or a solution of a sulphate ; a white precipitate of lead sulphate, $PbSO_4$, is produced.

Lead sulphate is slightly soluble in concentrated acids, and in solutions of some potassium and sodium salts ; it is insoluble n acetic acid. It is readily dissolved by solution of ammonium acetate, the resulting liquid yielding the ordinary reactions with soluble chromates and iodides. It also dissolves readily in solution of ammonium tartrate in presence of ammonia.

In dilute solutions the above reaction with sulphuric acid or a soluble sulphate does not take place immediately; the precipitate, however, falls after a time; its formation may be hastened by evaporating the mixture nearly to dryness and then diluting, or by adding to the mixture its own volume of alcohol.

The white precipitate often noticed in the vessels in which dilute commercial sulphuric acid is kept, is lead sulphate derived from the leaden chambers in which the acid is made. Its solubility in concentrated and its insolubility in dilute sulphuric acid explains its precipitation.

Antidotes.—From the insolubility of lead sulphate in water, the best *antidote*, in a case of poisoning by the acetate or other soluble lead salt, is a soluble sulphate, such as Epsom salt, sodium sulphate, or alum, vomiting being also induced, or the stomach-pump, or stomach-siphon, applied as quickly as possible.

Other tests for lead will be found in the reactions with *potassium iodide* (*see* p. 252); with *alkali-metal carbonates*, which produce white hydroxycarbonate, $2PbCO_3,Pb(OH)_2$, insoluble in excess; with *alkalies*, which yield a white precipitate of lead hydroxide, $Pb(OH)_2$, more or less soluble in excess; and with *alkali-metal phosphates*, *arsenates*, *ferrocyanides*, and *cyanides*, which form compounds mostly insoluble, but of no special analytical interest. Insoluble salts of lead may be dissolved by solution of caustic potash, KOH, or caustic soda, NaOH.

The metal is precipitated in a beautifully crystalline state by introducing metallic zinc (and some other metals) into a solution of a lead salt; the *lead tree* is thus formed.— Solid lead compounds are reduced when heated by the blowpipe-flame in a small cavity in a piece of charcoal, a soft malleable bead of metal being produced, and a yellowish ring of lead oxide deposited on the charcoal.

QUESTIONS AND EXERCISES

Write down equations representing the smelting of galena.—Mention some of the alloys of lead.—How is litharge produced?—Give the formulæ of white lead and red lead.—Describe the manufacture of white lead.—Draw a diagram showing the formation of Lead Acetate.—Describe the preparation and composition of *Liquor Plumbi Subacetatis*, B.P.—What is the action of nitric acid on red lead, litharge, and lead?—How is the official Lead Iodide prepared?—Describe the reaction between lead oxide, water, and olive-oil, at the temperature of boiling water, and give chemical formulæ explanatory of the composition of the products.—Mention the chief tests for lead.—How would you search for soluble compounds of lead in a domestic water supply?—What is the composition of chrome yellow and of chrome orange?—Name the best antidote in cases of poisoning by lead salts, and explain its mode of action.

BISMUTH: Bi. Atomic weight, 207·3

Occurrence.—Bismuth occurs in the metallic state in nature. It is freed from adherent quartz, etc., by simply heating, when the metal melts, runs off, and is collected in appropriate vessels. It is also met with in combination with other elements; most commonly, as oxide, Bi_2O_3, in *bismuth ochre;* sometimes, as sulphide, Bi_2S_3, in *bismuth glance.* Bismuth is greyish white in colour. In its general chemical relationships it is allied to the elements of the antimony and arsenium group, although in its analytical behaviour it is more closely related to lead and copper.

Purification.—Arsenium may be removed from melted bismuth by stirring it with an iron rod, iron arsenide rising to the surface of the mass: antimony by stirring in some bismuth oxide, when antimony oxide separates. Other metals present in bismuth, especially copper, are converted into sulphides, while bismuth is not affected, by fusing the crude metal with about five per cent. of potassium cyanide, and two per cent. of sulphur, the whole being well stirred for a quarter of an hour with a clay rod (stem of a tobacco-pipe). On pouring off the metal from the flux, and melting and stirring it with about five per cent. of a mixture of potassium and sodium carbonates, sulphur and traces of other impurities are removed, and the metal is obtained pure.—*Tamm.*

Uses.—Beyond the employment of some of its compounds in medicine, bismuth is but little used. Melted bismuth expands considerably on solidifying, and hence is valuable in taking sharp impressions of dies. It is a constituent of some kinds of type-metal and of pewter-solder.

Bismuth Nitrate

Experiment 1.—To a few drops of nitric acid and an equal quantity of water, in a test-tube, add a small quantity of powdered bismuth, heating the mixture if necessary; nitric oxide, NO, escapes, and solution of bismuth nitrate, $Bi(NO_3)_3$, results.

$$\underset{\text{Bismuth}}{Bi} + \underset{\text{Nitric acid}}{4HNO_3} = \underset{\text{Bismuth nitrate}}{Bi(NO_3)_3} + \underset{\text{Nitric oxide}}{NO} + \underset{\text{Water}}{2H_2O}$$

The solution, on evaporation, gives crystals, $Bi(NO_3)_3$, $5H_2O$, any arsenium which the bismuth may have contained remaining in the mother-liquor.

To make bismuth nitrate, oxynitrate, oxycarbonate (or other salts) on a larger scale, 2 ounces of the metal, in small fragments, are gradually added to a mixture of 4 fluid ounces of nitric acid and 3 of water, and, when effervescence (due to escape of nitric oxide) has ceased, the mixture is heated for ten minutes, poured off from any insoluble matter, evaporated to 2 fluid ounces to remove excess of acid, and then either set aside for crystals of nitrate to form, or poured into half a gallon of water to obtain bismuth oxynitrate, or into a solution of 6 ounces of ammonium carbonate in a quart of water to form oxycarbonate, as described in the following experiments.

The precipitates should be washed with cold water and dried at a temperature not exceeding 150° F. (65·5° C.). Exposed in the moist state to 212° F. (100° C.) for any considerable time, they undergo slight decomposition.

Bismuth Subnitrate or Oxynitrate

Experiment 2.—Pour some of the above solution of bismuth nitrate into a considerable quantity of water; decomposition occurs, and bismuth oxynitrate, $BiONO_3$, in a hydrous state, $BiONO_3$, H_2O (*Bismuthi Subnitras*, B.P.) is precipitated:—

$$\underset{\text{Bismuth nitrate}}{Bi(NO_3)_3} + \underset{\text{Water}}{2H_2O} = \underset{\text{Bismuth oxynitrate}}{BiONO_3,H_2O} + \underset{\text{Nitric acid}}{2HNO_3}$$

Filter, and test the filtrate for bismuth by adding excess of sodium carbonate; the formation of a precipitate shows that some bismuth still remains in solution.

Decomposition of bismuth nitrate by water is the ordinary process for the preparation of bismuth oxynitrate for use in medicine. For this purpose the original metal must contain no arsenium. In manufacturing the compound, therefore, before pouring the solution of nitrate into water, the liquid should be tested for arsenium by one of the hydrogen tests; if that element be present, the solution must be evaporated, and only the deposited crystals be used in the preparation of the oxynitrate. This must be done because on pouring an arsenical solution of bismuth nitrate into water, the arsenium is not wholly removed in the supernatant liquid unless the oxynitrate be redissolved and reprecipitated several times, according to the amount of arsenium present.

Bismuth subnitrate is gradually decomposed by solutions of alkali-metal carbonates (also by the bicarbonates, with production of carbonic anhydride), bismuth oxycarbonate and the alkali-metal nitrate being formed. It is sometimes administered in the form of a lozenge (*Trochiscus Bismuthi Compositus*, B.P.).

Bismuth Oxysalts.—On pouring a solution of bismuth chloride, $BiCl_3$, into water, bismuth oxychloride, $BiOCl$, is produced (a white powder used as a cosmetic, "pearl-white" (*Blanc de Perle*), also in enamels and in some varieties of sealing-wax). Bismuth bromide, $BiBr_3$, and iodide, BiI_3, similarly treated, yield oxybromide, $BiOBr$, and oxyiodide, $BiOI$. The subnitrate is, therefore, probably an analogous compound, an oxynitrate, $BiONO_3$. Bismuth sulphate, $Bi_2(SO_4)_3$, is also decomposed when placed in water, giving bismuth oxysulphate, $Bi_2O_2SO_4$.

It is difficult to prove whether or not the water in hydrous bismuth oxynitrate, $BiONO_3,H_2O$, is an integral part of the salt. If it is, the compound is probably bismuth hydroxynitrate, $Bi(OH)_2NO_3$.

Bismuth Oxide

Experiment 3.—Boil bismuth subnitrate with solution of caustic soda for a few minutes; it is converted into yellowish bismuth oxide, Bi_2O_3 (*Bismuthi Oxidum*, B.P.).

$$\underset{\substack{\text{Bismuth}\\\text{oxynitrate}}}{2BiONO_3} + \underset{\substack{\text{Sodium}\\\text{hydroxide}}}{2NaOH} = \underset{\substack{\text{Bismuth}\\\text{oxide}}}{Bi_2O_3} + \underset{\substack{\text{Sodium}\\\text{nitrate}}}{2NaNO_3} + \underset{\text{Water}}{H_2O}$$

Bismuth Subcarbonate or Oxycarbonate

Experiment 4.—To a solution of bismuth nitrate add solution of ammonium carbonate; a white precipitate of hydrous bismuth oxycarbonate, $2Bi_2O_2CO_3,H_2O$ (*Bismuthi Carbonas*, B.P.), is produced.

$$\underset{\substack{\text{Bismuth}\\\text{nitrate}}}{Bi(NO_3)_3} + \underset{\substack{\text{“Ammonium}\\\text{carbonate”}}}{2N_3H_{11}C_2O_5} + H_2O = \underset{\substack{\text{Ammonium}\\\text{nitrate}}}{6NH_4NO_3} + \underset{\substack{\text{Bismuth}\\\text{oxycarbonate}}}{Bi_2O_2CO_3} + \underset{\substack{\text{Carbonic}\\\text{anhydride}}}{3CO_2}$$

This compound may be regarded as similar in constitution to the oxysalts just described which are commonly looked upon as salts of a hypothetical radical *bismuthyl* (BiO).

Bismuth Citrate

Experiment 5.—To a nitric acid solution of bismuth nitrate add water, with frequent shaking, until a slight cloudiness of oxynitrate remains undissolved; then add solution of sodium citrate; warm and stir the mixture; set aside to cool; collect on a filter, wash, and dry the precipitated bismuth citrate, $BiC_6H_5O_7$.

$$\underset{\substack{\text{Bismuth}\\\text{nitrate}}}{Bi(NO_3)_3} + \underset{\substack{\text{Sodium}\\\text{citrate}}}{Na_3C_6H_5O_7} = \underset{\substack{\text{Bismuth}\\\text{citrate}}}{BiC_6H_5O_7} + \underset{\substack{\text{Sodium}\\\text{nitrate}}}{3NaNO_3}$$

Experiment 6.—To moist bismuth citrate (prepared by interaction between bismuth oxynitrate dissolved in nitric acid, and potassium citrate and carbonate) add ammonia until the precipitate is just dissolved; the solution of bismuth and ammonium citrate thus obtained, when of a strength of 800 grains of citrate in a pint, is official (*Liquor Bismuthi et Ammonii Citratis*, B.P.) shortly termed *Liquor Bismuthi.*

Bismuth Salicylate

Experiment 7.—To a solution of bismuth nitrate add a solution of sodium salicylate; a white precipitate of bismuth oxysalicylate, $C_6H_4{\cdot}OH{\cdot}COO{\cdot}BiO$ (*Bismuthi Salicylas*, B.P.), is produced.

Analytical Reactions of Bismuth Salts.

1. Through a solution of a bismuth salt (a slightly acid solution of nitrate, for example) pass hydrogen sulphide; a

black precipitate of bismuth sulphide, Bi_2S_3, is produced. Add solution of ammonia (to neutralize the acid) and then ammonium hydrosulphide; the precipitate, unlike As_2S_3 and Sb_2S_3, is insoluble.

2. Concentrate almost any acid solution of a bismuth salt and pour into much water containing some sodium or ammonium chloride; a white precipitate of bismuth oxychloride results.

This reaction is characteristic of bismuth salts. Bismuth oxychloride is specially insoluble in water, and is distinguished from antimonious oxychloride by being insoluble in solution of tartaric acid.

3. To a solution of a bismuth salt add a caustic alkali; a white precipitate of bismuth hydroxide, $Bi(OH)_3$, is produced, insoluble in excess, and becoming yellowish on boiling.

4. First prepare a reagent as follows:—Dissolve 1 grain of lead acetate in 3 ounces of hot water and add 30 drops of acetic acid; dissolve 60 grains of potassium iodide in 3 ounces of water; mix the solutions; on cooling, lead iodide is deposited in the characteristic yellow crystalline plates or scales. Next, place some of the reagent (crystals included) in a test-tube and heat gradually till solution takes place. Any liquid containing, or supposed to contain, bismuth is then added, and the whole allowed to cool. The separated scales will show a distinct change in colour from the original yellow to dark orange or crimson, according to the quantity of bismuth present.

Test for calcium phosphate in bismuth salts.—Dissolve the powder in nitric acid, add about twice its weight of citric acid and sufficient ammonia to give decided alkalinity; then boil, keeping the mixture faintly alkaline with ammonia; bismuth remains in solution, and calcium phosphate is precipitated.

Tests for other impurities in bismuth or its salts.—Dissolve in nitric acid; concentrate and set aside for crystals of bismuth nitrate to separate; pour off the mother-liquor, which will contain any impurities in a concentrated form. If this mother-liquor be evaporated with hydrochloric acid until all the nitric acid is dissipated, a little of the product should yield no evidence of arsenium on being examined by Marsh's test; no blue coloration on adding water and excess of ammonia (copper), and no precipitate on filtering and saturating the ammoniacal filtrate with nitric acid (silver); no white precipitate with dilute sulphuric acid (lead); no red or black precipitate with sodium sulphide (tellurium or selenium); and no blue precipitate with potassium ferrocyanide (iron).

CADMIUM: Cd. Atomic weight, **111·6**

In most of its chemical relations cadmium resembles zinc. In nature it occurs chiefly as an occasional constituent of the ore of that metal. In distilling zinc containing cadmium, the latter, being the more volatile, passes over first. In analytical operations cadmium, unlike zinc, comes down among the metals precipitated by hydrogen sulphide; that is, its sulphide is insoluble in highly dilute hydrochloric acid, while zinc sulphide is soluble. It is a white malleable metal which boils about 770° C. Sp. gr. 8·6.

Beyond the occasional employment of the sulphide as a pigment (*jaune brilliant*), and of the iodide and bromide in photography, cadmium and its salts are but little used.

Cadmium Iodide

Experiment.—Digest together, in a flask, metallic cadmium, warm water, and iodine, until the colour of the iodine disappears; solution of cadmium iodide, CdI_2, remains. Glistening white crystalline scales may be obtained on evaporating the solution.

This salt is employed with other iodides in iodizing collodion for photographic use. It readily melts; and it is soluble in water or alcohol, the solution reddening litmus.

Analytical Reactions of Cadmium Salts.

1. Through a solution of a cadmium salt (CdI_2 or $CdCl_2$) pass hydrogen sulphide; a yellow precipitate of cadmium

sulphide, CdS, is produced, resembling in appearance arsenious, arsenic, and stannic sulphides. Add ammonium hydrosulphide; the precipitate, unlike the sulphides just mentioned, does not dissolve. It dissolves easily in hot dilute hydrochloric or sulphuric acid.

Cadmium and cupric sulphides may be separated by means of solution of potassium cyanide, in which cupric sulphide is soluble and cadmium sulphide insoluble.

2. To a solution of a cadmium salt add solution of caustic potash; a white precipitate of cadmium hydroxide, $Cd(OH)_2$, is produced, insoluble in excess of the precipitant.

Zinc hydroxide, $Zn(OH)_2$, precipitated under similar circumstances, is soluble in solution of caustic potash; the filtrate from the cadmium hydroxide may therefore be tested for any zinc, present as an impurity, by adding hydrogen sulphide or ammonium hydrosulphide. Zinc and cadmium hydroxides are soluble in excess of solution of ammonia.

Before the blowpipe-flame, on charcoal, cadmium salts give a brown deposit of cadmium oxide, CdO.

QUESTIONS AND EXERCISES

How does bismuth occur in nature?—What is the quantivalence of bismuth?—Write equations descriptive of the action of nitric acid on bismuth, and water on bismuth nitrate.—How may arsenium be excluded from bismuth salts?—Give an equation illustrating the process for the preparation of bismuth carbonate.—Write formulæ showing the accordance in molecular constitution of the official oxynitrate and oxycarbonate with the other bismuth salts, and with ordinary nitrates and carbonates.—How is *Liquor Bismuthi et Ammonii Citratis* prepared?—Mention the tests for bismuth.—In what condition does cadmium occur in nature?—By what process may cadmium iodide be prepared?—Mention the chief test for cadmium.—Distinguish cadmium sulphide from sulphides of similar colour.—How is cadmium separated from zinc?

SILVER: Ag. Atomic weight, 107·11

Occurrence.—This element occurs in nature in the metallic state; and also combined with sulphur as silver sulphide, Ag_2S, associated with much lead sulphide, forming *argentiferous galena*.

Preparation.—The lead obtained from argentiferous galena is melted and slowly cooled; crystals of nearly pure lead separate first and are raked out from the still fluid mass, which thus consists of an alloy richer in silver. The operation is repeated several times until an alloy very rich in silver is finally obtained; this is roasted in a current of air, whereby the lead is oxidized and removed as litharge, while pure silver remains. Other ores undergo various preparatory treatments according to their nature, and are then shaken with mercury, which amalgamates with and dissolves the particles of metallic silver, the mercury being subsequently removed from the amalgam by distillation. Soils and minerals containing metallic silver are also treated in this way. An important improvement in the amalgamation process, by which the mercury more readily unites with the silver, consists in the addition of a small proportion of sodium to the mercury. Silver chloride may be dissolved from ores by solution of sodium thiosulphate.

Silver is not readily affected by the weak acid or other fluids of food, though it is rapidly tarnished by sulphur and many sulphur compounds. It does not perceptibly attack hydrochloric acid; it reduces somewhat diluted nitric acid to nitric oxide, NO, silver nitrate, $AgNO_3$, being formed; it also reduces hot sulphuric acid to sulphurous anhydride, SO_2, silver sulphate, Ag_2SO_4, being formed. The latter salt is crystalline, and slightly soluble in water.

Impure Silver Nitrate

Experiment 1.—Dissolve a silver coin in nitric acid; nitric oxide, NO, is evolved, and a solution of silver and cupric nitrates is obtained.

Silver Coinage.—Pure silver is too soft for use as coin; it is therefore hardened by alloying with copper. British silver money contains 7·5, German 25, and French 10 and 16·5 per cent. of copper—for the fineness of the French standard silver is 0·900 in the five-franc piece, while an inferior alloy of 0·835 is used for the coins of lower denominations. The one-franc piece, composed of the latter alloy, is still made to weigh five grammes, the weight originally chosen for the franc as the unit of the monetary scale when the fineness of the coin was 0·900. It has now become a token, like the British shilling, of which the nominal value exceeds the intrinsic value. One pound troy of British standard silver is coined into 66 shillings, of which the metal is worth from 25s. to 30s., less or more, according to the market price of silver. The standard fineness of this silver is 0·925, *i.e.*, 3 of copper in 40 of the alloy.

Silver Chloride

Experiment 2.—To the product obtained in the preceding experiment, add water and hydrochloric acid or a soluble chloride; a white precipitate of silver chloride, $AgCl$, is produced, copper still remaining in solution. Collect the precipitate on a filter and wash it with water; it is pure silver chloride.

Notes.—The copper may also be separated by evaporating the solution of the metals in nitric acid to dryness and gently heating the residue, when the cupric nitrate is decomposed but the silver nitrate is unaffected. The latter may be dissolved out from the residual cupric oxide by means of water.

Silver chloride may be obtained in crystals by evaporation of its solution in ammonia.

The usefulness of halogen salts of silver in photography depends upon the fact that these compounds undergo a darkening on exposure to light. According to Baker, this is due to the formation of an oxy-compound—in the case of the chloride, Ag_2ClO.

Pure Silver

Experiment 3.—Place the silver chloride obtained in experiment 2 in a dish, wet it with dilute sulphuric acid, and lay a piece of sheet zinc on the mixture; metallic silver is precipitated and, after about one day, wholly removed from combination. Collect the precipitate on a filter and wash with water; it is pure metallic silver, and is readily fusible into a single button, especially if mixed with a little borax and nitre.

Note.—Any considerable quantity of silver chloride may be reduced to a lump of the metal by fusion, in a crucible, with about half its weight of sodium carbonate. The chloride is also reduced by boiling it with caustic alkali and grape sugar until a trial sample is entirely dissolved by nitric acid.

Pure Silver Nitrate

Experiment 4.—Dissolve the pure silver from experiment 3 in nitric acid (3 parts by weight of silver require about 2 or $2\frac{1}{2}$ of concentrated acid diluted with 5 of water), and remove excess of acid by evaporating the solution to dryness and slightly heating the residue; the product is pure silver nitrate. Dissolve it by heating with a small quantity of water; the solution on cooling, or on evaporation, deposits colourless tabular crystals of silver nitrate.

$$\underset{\text{Silver}}{3Ag} + \underset{\text{Nitric acid}}{4HNO_3} = \underset{\text{Nitric oxide}}{NO} + \underset{\text{Silver nitrate}}{3AgNO_3} + \underset{\text{Water}}{2H_2O}$$

Notes.—Silver Nitrate (*Argenti Nitras*, B.P.), "is prepared by the interaction of nitric acid and silver." The salt, fused and poured into proper moulds, yields the white cylindrical sticks or rods commonly termed *caustic* (from *καίω*, *kaiō*, I burn), or *lunar caustic*. (The alchemists called silver *Diana* or *Luna*, from its supposed mysterious connection with the moon.) Tough "caustic points" contain 5 per cent. of potassium nitrate, the product being the officially recognised *Argenti Nitras Induratus*, B.P., or "Toughened Caustic." "Mitigated Caustic," *Argenti Nitras Mitigatus*, B.P., is a fused mixture of one part of silver nitrate with two parts of potassium nitrate.

The specimen of silver nitrate obtained in the foregoing experiment, dissolved in water, will be found useful as an analytical reagent. Silver nitrate dissolves in 90 per cent. alcohol; but decomposition occurs after a time.

Silver salts are decomposed when in contact with organic matter, especially on exposure to light, or on heating, the metal itself being liberated, or a black insoluble compound formed. Hence the value of silver nitrate in the manufacture of indelible ink for marking linen; hence, too, the reason of the practice of rendering silver solutions clear by subsidence and decantation, rather than by filtration through paper; and hence the cause of those cases of actual combustion which have been known to occur in preparing pills containing silver oxide and essential oil or other organic matter. Linen marked with silver marking-ink should not be cleansed by aid of bleaching liquor, as the marked parts are then apt to be rapidly oxidized and "tendered," holes resulting. Paul says the reaction is as follows:— $Ag_2O + CaCl_2O_2 = 2AgCl + CaO + O_2$.

Silver Oxide

Experiment 5.—To a solution of silver nitrate add solution of caustic potash or caustic soda, or lime-water; an olive-brown precipitate of silver oxide, Ag_2O, is produced. The washed and dried oxide is decomposed by the action of heat, with production of metal. It is also reduced by contact with organic matter. (*See* preceding paragraph.)

Argenti Oxidum, B.P., is prepared as above, calcium hydroxide being the precipitant employed, caustic soda or caustic potash not being so readily removed by washing. Three and a half pints of good lime-water will decompose half an ounce of silver nitrate.

$$\underset{\substack{\text{Silver}\\ \text{nitrate}}}{2AgNO_3} + \underset{\substack{\text{Calcium}\\ \text{hydroxide}}}{Ca(OH)_2} = \underset{\substack{\text{Silver}\\ \text{oxide}}}{Ag_2O} + \underset{\substack{\text{Calcium}\\ \text{nitrate}}}{Ca(NO_3)_2} + \underset{\text{Water}}{H_2O}$$

Silver oxide is also precipitated on adding ammonia to a solution of silver nitrate, but it is rapidly taken up by the ammonium nitrate formed at the same time, argentammonium nitrate, NH_3AgNO_3, probably being formed. The direct solution of silver oxide in ammonia may give the highly explosive substance known as Berthollet's fulminating silver (? NH_2Ag). Ordinary *fulminating silver*, $C_2N_2O_2Ag_2$, results from the interaction of silver nitrate, nitric acid, and alcohol. The corresponding mercury compound, *fulminating mercury*, $C_2N_2O_2Hg$, is used in percussion caps. *Solution of silver ammonio-nitrate*, B.P., is official, as a reagent.

Methods of forming several other salts of silver are incidentally mentioned in the following analytical paragraphs.

Analytical Reactions of Silver Salts.

To a solution of a silver salt add hydrochloric acid or other soluble chloride; a white curdy precipitate of silver chloride, AgCl, is produced. Add nitric acid, and boil; the precipitate does not dissolve. Pour off the acid and add solution of ammonia; the precipitate dissolves. Neutralize the ammoniacal solution by means of an acid; the white curdy precipitate is reproduced.

This is the most characteristic test for silver. The precipitated chloride is also soluble in solutions of sodium thiosulphate or potassium cyanide—facts of considerable importance in photographic operations.

Other analytical reagents besides the above are occasionally useful.——Hydrogen sulphide, or ammonium hydrosulphide, gives a black precipitate of silver sulphide, Ag_2S, insoluble in alkalies.——Solution of caustic potash or of caustic soda gives a brown precipitate of silver oxide, Ag_2O.——Sodium phosphate gives a yellow precipitate of silver phosphate, Ag_3PO_4, soluble in nitric acid and in solution of ammonia. ——Ammonium arsenate gives a brown precipitate of silver arsenate, Ag_3AsO_4, already noticed in connection with arsenic acid.——Potassium bromide gives a yellowish-white precipitate of silver bromide, AgBr, insoluble in dilute acids, soluble with some difficulty in ammonia.——Potassium iodide produces a pale-yellow precipitate of silver iodide, AgI (*Argenti Iodidum,* U.S.P.), insoluble in dilute acids. It is changed by ammonia into a yellowish insoluble compound. ——Potassium cyanide gives a white precipitate of silver cyanide, AgCy (*Argenti Cyanidum,* U.S.P.), soluble in excess, somewhat soluble in ammonia, insoluble in dilute nitric acid, soluble in boiling concentrated nitric acid.—— Potassium chromate, K_2CrO_4, gives a red precipitate of silver chromate, Ag_2CrO_4. ——Potassium bichromate gives a red precipitate of silver anhydrochromate, $Ag_2Cr_2O_7$.——Many organic acids give rise to insoluble silver salts.——Several metals displace silver from solution, mercury forming in this way a crystalline precipitate known as the silver tree, or *Arbor Dianæ.*——Heated on charcoal with sodium carbonate in the blowpipe-flame, silver salts yield bright globules of silver, not accompanied by an incrustation as in the corresponding reaction with lead salts ; the experiment may be performed with the nitrate, which first melts, and then, like all nitrates, deflagrates, yielding a white metallic coating of silver which slowly aggregates to a button.

Antidotes.—Solution of common salt, sal-ammoniac, or any other inert chloride should obviously be administered where large doses of silver nitrate have been swallowed. A quantity of sea-water or brine would convert the silver into insoluble chloride, and at the same time produce vomiting.

QUESTIONS AND EXERCISES

By what process is silver obtained from argentiferous lead?—What weight of English silver coin will yield one pound of pure silver nitrate?—How may the metal be recovered from impure silver salts?—Give a diagram showing the formation of silver nitrate.—Describe the reaction of solution of lime with silver nitrate.—Mention the chief test for silver, and state how silver salts may be distinguished from those of lead and mercury.—Name the antidote for silver.

Qualitative Analysis.

Methods for the qualitative analysis of solutions containing any or all of the metals, copper, mercury (either as mercurous or as mercuric salt), tin (as stannous salt), lead, bismuth, cadmium, and silver have now to be considered. Before introducing the student to the systematic examination of solutions containing any or all of the metals of general interest, treated of in this Manual, it will be convenient to indicate how the particular metals just mentioned above, are dealt with in that systematic examination, in so far as dividing them into analytical groups is concerned.

The first point to be noted is that silver and mercurous chlorides are insoluble, and that lead chloride is only sparingly soluble, in cold water. Addition of excess of hydrochloric acid, or other soluble chloride, to the solution, causes the complete precipitation of silver and mercurous chlorides (or, if no precipitate forms, shows the absence of these metallic radicals), and it may cause the precipitation of some lead chloride also. After removing any precipitate by filtration, part or the whole of the lead (if any was present originally), and the whole of any of the other metals mentioned above, which may have been present, pass into the filtrate, from which they can be precipitated by means of hydrogen sulphide.

The fact that this method of dividing these metals into two groups for analytical purposes, is practically universally employed, furnishes the explanation for the separate treatment of the metallic radicals constituting the two groups, in the two pairs of preliminary analytical schemes which follow (pp. 269-272). The first pair of schemes deal with silver, mercurous, and lead salts; while the second pair deal with cupric, mercuric, lead, bismuth, and cadmium salts, and partially with stannous salts.

The position of tin in this analytical arrangement is somewhat anomalous, since, in the course of the systematic separation of the metals, this element falls into the analytical group along with arsenium and antimony. The connection of this latter group (the arsenium group) with the group embracing copper, bismuth, etc. (the copper group), will be evident later, when the scheme for the systematic separation of the whole of the metals of general interest comes to be discussed (p. 274).

DIRECTIONS FOR APPLYING SOME OF THE REACTIONS DESCRIBED IN THE FOREGOING PARAGRAPHS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF A SALT OF ONE OF THE METALS SILVER, MERCURY (AS MERCUROUS SALT), LEAD.

Add hydrochloric acid :—

Silver is indicated by a white curdy precipitate, insoluble in excess, easily soluble in ammonia.

Mercurous salt is indicated by a white precipitate which is turned black by ammonia.

Lead is indicated by a white precipitate, insoluble in ammonia. Confirm by boiling a small portion of the hydrochloric-acid precipitate in water; it dissolves.

If hydrochloric acid gives no precipitate, silver and mercurous salts are absent, and lead can only be present in very small quantity. The presence of lead in small quantity is best detected by applying the sulphuric acid test to a fresh portion of the original solution, the tube being set aside for a time if the precipitate does not appear at once.*

TABLE OF SHORT DIRECTIONS FOR APPLYING SOME OF THE REACTIONS DESCRIBED IN THE FOREGOING PARAGRAPHS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ANY OR ALL OF THE METALS SILVER, MERCURY (AS MERCUROUS SALT), LEAD.

Add hydrochloric acid in excess, filter, and wash the precipitate with a small quantity of cold water.

<table>
<tr><td colspan="3">Precipitate
Pb Hg (ous) Ag
Wash on the filter with boiling water.</td><td rowspan="3">Filtrate
Pb
Add
H_2SO^4
white ppt.*</td></tr>
<tr><td colspan="2">Residue
Hg (ous) Ag
Add NH_4OH.</td><td rowspan="2">Filtrate
Pb
Add
H_2SO_4
white ppt.*</td></tr>
<tr><td>Residue
Hg
(mercurous), black</td><td>Filtrate
Ag
Add HNO_3 white ppt.</td></tr>
</table>

DIRECTIONS FOR APPLYING SOME OF THE REACTIONS DESCRIBED IN THE FOREGOING PARAGRAPHS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF A SALT OF ONE OF THE METALS COPPER, MERCURY (AS MERCURIC SALT), TIN (AS STANNOUS SALT), LEAD, BISMUTH, CADMIUM.

Note that solutions of cupric salts have a blue colour.

Acidulate the liquid with hydrochloric acid and pass hydrogen sulphide through it until the mixture, after shaking, smells of the gas:—

---

* Liquids containing only a small quantity of lead do not readily yield lead sulphate on the addition of sulphuric acid. Before lead can be said to be absent, therefore, the liquid should be evaporated to dryness with one drop of sulphuric acid, and the residue digested in water; any lead sulphate then remains as a heavy, white, insoluble powder.

Cadmium salts give a yellow precipitate, insoluble in ammonia, easily soluble in hot dilute hydrochloric acid.

Cupric, mercuric, stannous, lead, and bismuth salts give dark-brown or black precipitates. In the case of a mercuric salt, the precipitate may be white or pale-yellow at first, but it rapidly becomes orange, brown, and, finally, black. In the case of a lead salt, the precipitate is sometimes reddish-brown if much hydrochloric acid is present, but it becomes black on dilution of the solution and addition of enough hydrogen sulphide.

To distinguish cupric, mercuric, stannous, lead, and bismuth salts from one another, add potassium iodide to another portion of the original solution:—

A pale-brownish mixture (which really consists of a nearly colourless precipitate of cuprous iodide in a yellow or brown solution of iodine) indicates a cupric salt. The brown colour disappears and the precipitate is seen to be nearly colourless, when solution of sulphurous acid is added. Compare reaction 7, p. 232.

A yellowish-red precipitate, rapidly becoming bright-red, soluble in excess of potassium iodide, indicates a mercuric salt.

The production of a pale-yellow precipitate, or, in dilute solutions, of none at all, indicates a stannous salt.

A yellow precipitate, insoluble in excess of potassium iodide, soluble in boiling water, indicates a lead salt.

A bright-yellow solution, or a brown precipitate which dissolves in excess of potassium iodide to form a bright-yellow solution, indicates a bismuth salt.

TABLE OF SHORT DIRECTIONS FOR APPLYING SOME OF THE REACTIONS DESCRIBED IN THE FOREGOING PARAGRAPHS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF TWO OR MORE OF THE METALS, COPPER, MERCURY (AS MERCURIC SALT), LEAD, BISMUTH, CADMIUM.

Acidulate the liquid with hydrochloric acid and pass hydrogen sulphide through it until the mixture, after shaking, smells of the gas ; filter.

<table>
<tr><td colspan="4">Precipitate
Cu Hg (ic) Pb Bi Cd *
Wash with water ; boil with HNO_3 ; dilute with water and filter.</td><td rowspan="4">Filtrate
Dilute with H_2S solution so as to ensure complete precipitation of Pb, Bi, Cd, the sulphides of which are to some extent soluble in cold dilute HCl.
If any further precipitate is produced, it may be added to the original precipitate, or examined separately.</td></tr>
<tr><td rowspan="3">Residue
Hg (ic)
Black.
Confirm by Cu test in original solution.</td><td colspan="3">Filtrate
Cu Pb Bi Cd
Add NH_4OH in excess, filter.</td></tr>
<tr><td colspan="2">Precipitate
Pb Bi
Wash, dissolve on filter in a few drops of dilute HNO_3, dilute, filter.</td><td>Filtrate
Cu Cd
(Blue if Cu present).
Add KCN in excess, and pass H_2S.</td></tr>
<tr><td>Ppt.
Bi
white</td><td>Filtrate
Pb
Add H_2SO_4, set aside, white ppt.</td><td>Ppt.
Cd
yellow

Filtrate
Cu
Acidify with acetic acid. Brown ppt.</td></tr>
</table>

---

* The possible presence of tin, whether as stannous or as stannic salt, is not considered in the separation described here, since, in the systematic examination of a solution which might contain tin along with copper, mercury, etc., any stannous or stannic sulphide is removed from the cupric, mercuric, etc., sulphides before the examination of the latter sulphides is proceeded with. (*See* p. 274.)

The Analytical Classification of Metals.
Systematic Analysis.

The following Tables, giving directions for the analytical examination of solutions for the presence of practically any of the metallic radicals hitherto considered, include and, to a certain extent, epitomize the Tables previously given under the different groups. The order of addition of the group-reagents is arranged according to a carefully devised plan which is set forth in the following outline of the annexed analytical Tables :—

HCl	H_2S		NH_4SH		$(NH_4)_2CO_3$	$(NH_4)_2HPO_4$	
Ag	Cd	Insoluble in NH_4SH+S	Zn	Hydroxides soluble in NH_4OH	Ba	Mg	K
	Cu		Mn*				
Hg (as mercurous salt)	Hg (as mercuric salt)		Co		Sr		Na
Pb (partially)	Pb (entirely)		Ni		Ca		NH_4
	Bi		Al	Hydroxides insol. in NH_4OH			Li
	As (as arsenious or arsenic salt)	Soluble in NH_4SH+S	Fe				
	Sb		Cr				
	Sn (as stannous or stannic salt)						
	Au						
	Pt						

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* *See* Experiment 5, p. 151.

Note.—The student should practise the examination of aqueous solutions of salts of the above metals, by aid of the Tables, until he is able to ascertain with facility and accuracy which metallic radicals are present. In this way he will best perceive the peculiarities of each element, and the general relations of the elements to each other.

The foregoing outline indicates that hydrochloric acid, which is the first group-reagent added, precipitates silver and mercurous chlorides and partially precipitates lead chloride (unless the lead solution is very dilute). The filtrate obtained on removing the hydrochloric acid precipitate is next treated with hydrogen sulphide, which precipitates the metals of the copper and arsenium groups together as sulphides. The sulphides of these two groups behave differently when digested with *yellow* ammonium hydrosulphide (or, what comes to the same thing, ammonium hydrosulphide and a pinch of sulphur), those of the arsenium group dissolving in this reagent, while those of the copper group remain undissolved. (*See* note on p. 272.) Hence, when the sulphides of the two groups have been precipitated together and filtered off, the mixed precipitate is treated with yellow ammonium hydrosulphide so as to effect the separation of the arsenium group sulphides from the copper group sulphides, while the filtrate still contains the metals of the iron, zinc, and barium groups, along with magnesium and the alkali metals.

A very common mode of dealing with the filtrate (and the one adopted in the annexed Tables) is to add excess of ammonia and then ammonium hydrosulphide to it. The ammonia first neutralizes the hydrochloric acid present in the filtrate, forming with it ammonium chloride :—$HCl + NH_4OH = NH_4Cl + H_2O$; and as soon as this action has been completed, it forms some ammonium hydrosulphide with the excess of hydrogen sulphide present. This, together with more ammonium hydrosulphide which is added, precipitates, as sulphides or hydroxides, all the metals of the iron and zinc groups. The ammonium chloride, formed by the first interaction of the ammonia with the hydrochloric acid, prevents the precipitation of magnesium at this stage. The metals of the barium group, along with magnesium and the alkali metals, pass into the filtrate. The barium group metals are subsequently precipitated as carbonates by the addition of ammonium carbonate; and magnesium and, to some extent, lithium as phosphates by means of ammonium phosphate, as already described on p. 136, where the mode of dealing with the other alkali-metals is also discussed.

TABLE OF SHORT DIRECTIONS FOR THE ANALYSIS OF AN AQUEOUS OR ONLY SLIGHTLY ACID SOLUTION OF ORDINARY SALTS OF ONE OF THE METALS HITHERTO CONSIDERED.

Add hydrochloric acid.

<table>
<tr>
<td rowspan="7">Precipitate
Hg(ous) Pb Ag
Collect, wash, and add NH_4OH.
Hg ppt., blackened.
Pb ppt., still white.
Ag ppt., dissolved.
Sb and Bi may also be precipitated by HCl, but are dissolved on adding more HCl.</td>
<td colspan="7">If HCl gave no precipitate, pass H_2S through the solution.</td>
</tr>
<tr>
<td rowspan="6">Precipitate
Cd Cu Hg(ic) Pb Bi As Sb Sn Au Pt
Collect, wash, add NH_4SH and S, and warm.
Insoluble
Cd, yellow
$\left.\begin{array}{l}\text{Cu}\\ \text{Hg(ic)}\\ \text{Pb}\\ \text{Bi}\end{array}\right\}$ black
Soluble
$\left.\begin{array}{l}\text{As (ous \& ic)}\\ \text{Sn (ic)}\end{array}\right\}$ yellow
Sb, orange
$\left.\begin{array}{l}\text{Sn (ous)}\\ \text{Au}\\ \text{Pt}\end{array}\right\}$ black
Apply special tests for each to the original solution. For these *see* the previous pages.</td>
<td colspan="6">If H_2S gave no precipitate, add NH_4Cl, NH_4OH, and NH_4SH.</td>
</tr>
<tr>
<td rowspan="5">Precipitate
Zn Mn Co Ni Al Fe Cr
$\left.\begin{array}{l}\text{Zn}\\ \text{Al}\end{array}\right\}$ white
Cr, green
Mn, skin-tint
$\left.\begin{array}{l}\text{Ni}\\ \text{Co}\\ \text{Fe}\end{array}\right\}$ black
Test specially for each in original solution. *See* previous pages.</td>
<td colspan="5">If NH_4SH gave no precipitate, add $(NH_4)_2CO_3$</td>
</tr>
<tr>
<td colspan="3">Precipitate
Ba Sr Ca
Collect, wash, dissolve in $HC_2H_3O_2$, add K_2CrO_4</td>
<td colspan="2">If $(NH_4)_2CO_3$ gave no precipitate, add $(NH_4)_2HPO_4$.</td>
</tr>
<tr>
<td rowspan="2">Ppt.
Ba</td>
<td colspan="2">Sol.
Sr Ca
Add dil. H_2SO_4</td>
<td rowspan="3">Ppt.
Mg</td>
<td rowspan="3">If no precipitate, test original solution in flame on loop of Pt wire.
Li, crimson.
Na, yellow.
K, violet.
Also, test original solution for NH_4</td>
</tr>
<tr>
<td>Ppt.
Sr</td>
<td>Sol.
Ca</td>
</tr>
<tr>
<td colspan="3">Confirm Ba, Sr, Ca by flame-test.</td>
</tr>
</table>

Of the accompanying Tables, the first includes directions for the analysis of an aqueous or only slightly acid solution containing one salt of any of the metals hitherto considered. Here the colour of the precipitate or precipitates afforded by a metal under given circumstances must largely be relied on in attempting the detection of the various elements.

The folded Table is intended as a scheme for the analysis of solutions containing salts of more than one metal. It is a compilation from the foregoing reactions and may often be altered or varied in arrangement to suit the requirements of the analyst.

The analysis of solutions containing only one metal will serve to impress the memory with the characteristic tests for the various metals and other radicals, and familiarize the mind with chemical principles. More thorough analytical and general chemical knowledge is only acquired by working on such mixtures of bodies as are met with in actual practice, beginning with solutions which may contain any or all of the members of a group (*see* previous pages), then examining solutions containing more than one group, and finally analysing liquids in which are dissolved several salts of any of the common or rarer metals.

The Author cannot too strongly recommend students thoroughly to master the art of analysis, not only on account of its direct value, but because its practice enables them rapidly and soundly to acquire a good knowledge of Chemistry, and greatly to improve their general mental faculties.

General and Special Memoranda relating to the preceding Analytical Tables

General Memoranda.

These Tables are constructed for the analysis of salts more or less soluble in water.——The student has still to learn how substances insoluble in water are to be brought into a state of solution; but once dissolved, their analysis is effected by the same scheme as that just given. The Tables, especially the longer folded one, may therefore be regarded as fairly representing the method by which metallic constituents of chemical substances are separated from each other and recognised.

The group-reagents adopted in the Tables are *hydrochloric*

TABLE OF SHORT DIRECTIONS FOR APPLYING SOME OF THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS OR ONLY SLIGHTLY ACID SOLUTION OF ORDINARY SALTS OF **ANY OF THE METALS** OF GENERAL INTEREST.

Add hydrochloric acid.

<table>
<tr><td colspan="3">Precipitate
Hg(ous) Pb Ag
Wash, boil with water, filter.</td><td colspan="20">Filtrate
Cd Cu Hg(ic) Pb Bi As(ous)(ic) Sb Sn(ous)(ic) Zn Mn Co Ni Al Fe(ous)(ic) Cr Ba Sr Ca Mg Li K Na NH_4
Pass H_2S through the liquid, filter.</td></tr>
<tr><td colspan="2">Residue
Hg(ous) Ag
Wash, add NH_4OH.</td><td rowspan="5">Filtrate
Pb
Add H_2SO_4
White ppt.</td><td colspan="8">Precipitate
Cd Cu Hg(ic) Pb Bi As Sb Sn
Collect, wash, digest with NH_4SH and S, filter.</td><td colspan="12">Filtrate
Zn Mn Co Ni Al Fe Cr Ba Sr Ca Mg Li K Na NH_4
Add NH_4Cl, NH_4OH, and NH_4SH, warm gently, and filter.</td></tr>
<tr><td rowspan="4">Res.
Hg
(ous)
Black</td><td rowspan="4">Filtrate
Ag
Add
HNO_3.
White ppt.</td><td colspan="5">Precipitate
Cd Cu Hg(ic) Pb Bi
Wash, boil in HNO_3, filter.</td><td colspan="3">Filtrate
As Sb Sn
Add dilute HCl, filter, drain well, add concentrated HCl, boil, dilute slightly, filter.</td><td colspan="6">Precipitate
Zn Mn Co Ni Al Fe Cr
Collect, wash, dissolve in HCl, with a few drops of HNO_3, boil, add NH_4OH, stir, filter.</td><td colspan="6">Filtrate
Ba Sr Ca Mg Li K Na NH_4
Add $(NH_4)_2CO_3$, warm, filter.</td></tr>
<tr><td rowspan="3">Residue
Hg
(ic)
Black.
Confirm by Cu test in original solution.</td><td colspan="4">Filtrate
Cd Cu Pb Bi
Add NH_4OH, filter.</td><td rowspan="3">Residue
As
Yellow.
Confirm by Fleitmann's test.</td><td colspan="2">Filtrate
Sn Sb
Pour into H-apparatus.</td><td colspan="3">Precipitate*
Fe Al Cr
Wash, dry, fuse on Pt. foil with Na_2CO_3 and KNO_3, boil in water, and filter.</td><td colspan="3">Filtrate
Zn Mn Co Ni
Acidify with $HC_2H_3O_2$, pass H_2S, filter.</td><td colspan="3">Precipitate
Ba Sr Ca
Collect, wash, dissolve in $HC_2H_3O_2$, add excess of K_2CrO_4, filter.</td><td colspan="3">Filtrate
Mg Li K Na NH_4
Add $(NH_4)_2HPO_4$, stir, filter.</td></tr>
<tr><td colspan="2">Precipitate
Pb Bi
Wash, add a few drops HNO_3, dilute, filter.</td><td colspan="2">Filtrate
Cd Cu
Add KCy and H_2S.</td><td rowspan="2">Sn
remains on Zn.
Dissolve in HCl, and apply tests.</td><td rowspan="2">Sb
escapes as SbH_3.
Test as usual.</td><td rowspan="2">Residue
Fe_2O_3
brown.
Test original solution for ferrous or ferric state.</td><td colspan="2">Filtrate
If yellow, Cr present.
Divide into two parts.</td><td rowspan="2">Sol.
Mn
Add NH_4OH and NH_4SH
Buff, turning brown.
Search also for Mn in the Fe Al Cr ppt.</td><td colspan="2">Precipitate
Zn Co Ni
Boil with HCl and a little HNO_3; add KOH, filter.</td><td rowspan="2">Ppt.
Ba
Yellow</td><td colspan="2">Filtrate
Sr Ca
Add dilute H_2SO_4, let stand, filter.</td><td rowspan="2">Ppt.
Mg
White</td><td colspan="2">Filtrate
Li K Na NH_4
Evaporate to small bulk, add NH_4OH.</td></tr>
<tr><td>Ppt.
Bi
White.
See also pp. 279 and 280.</td><td>Filt.
Pb
Add H_2SO_4, set aside; white ppt.
See footnote to p. 270.</td><td>Ppt.
Cd
Yellow.</td><td>Filt.
Cu
Acidify with $HC_2H_3O_2$
Brown ppt.</td><td>Sol.
Al
Add excess of NH_4Cl and boil off NH_3.
White ppt.</td><td>Sol.
Cr
Add $HC_2H_3O_2$ and excess of $AgNO_3$; red ppt.
Or boil with H_2SO_4 and alcohol.
Green sol.</td><td>Filt.
Zn
Add NH_4SH.
White ppt.</td><td>Precipitate
Co Ni
Dissolve in HCl and proceed as directed on p. 156.</td><td>Ppt.
Sr
White</td><td>Filt.
Ca
Add NH_4OH and $(NH_4)_2C_2O_4$
white ppt.</td><td>Ppt.
Li
See p. 281.</td><td>Filtrate
K Na NH_4
Evaporate, ignite, dissolve.
Test for K by H_2PtCl_6, or by Carnot's test, p. 82,
Na by flame,
NH_4 in original solution.</td></tr>
<tr><td colspan="3">*See* also p. 278.</td><td colspan="5"></td><td colspan="3">*See* also p. 279.
Au and Pt are specially sought when necessary.</td><td colspan="3">*See* also p. 280.
* Test this also for Mn by Crum's process, p. 151.</td><td colspan="3"></td><td colspan="3">*See* also page 281, and the more delicate separation given on p. 136.</td><td colspan="3"></td></tr>
</table>

[*To face p.* 276.]

acid, hydrogen sulphide, ammonium hydrosulphide, ammonium carbonate, and *ammonium phosphate.* If a group-reagent produces no precipitate, it is evident that there can be no member of the group present. At first, therefore, add only a small quantity of a group-reagent, and if it produces no effect add no more; for it is not advisable to overload a solution with useless reagents; substances expected to come down as precipitates are not infrequently held in solution in the liquid by excess of acid, alkali, or concentrated aqueous solution of some group-reagent, thoughtlessly added. Indeed, experienced manipulators make preliminary trials with group-reagents on a few drops only of the liquid under examination; if a precipitate is produced, it is added to the bulk of the original liquid, and the addition of the group-reagent continued; if a precipitate is not produced, the few drops are thrown away, and the unnecessary addition of a group-reagent thus avoided altogether, an advantage fully making up for the extra trouble of making a preliminary trial.—While shunning excess, however, care must be taken to avoid deficiency; a substance only partially removed from solution through the addition of an insufficient amount of a reagent will appear where not expected, be constantly mistaken for something else, and cause much trouble. It is a good plan, when a group-reagent has produced a precipitate and the latter has been filtered off, to add a little more of the reagent to the clear filtrate; if more precipitate is produced, an insufficient amount of the group-reagent was introduced in the first instance; but the error is corrected by simply re-filtering; if no precipitate occurs, the mind is satisfied and the way cleared for further operations.

Group-precipitates, or any precipitates still requiring examination, should, as a rule, be well washed before further testing; this is to remove the aqueous solution of other substances adhering to the precipitate, so that subsequent reactions may take place between the reagent used and the precipitate only.—A precipitate is sometimes in so fine a state of division as to retard filtration by clogging the pores of the paper, or even to pass through the filter altogether; in these cases the mixture may be warmed or boiled (or a fresh quantity of the original solution may be warmed *before* the group-reagent is added), which usually causes aggregation of the particles of a precipitate, and hence facilitates the passage of liquids.

Division of Work.—It is immaterial whether a solution be first divided into group-precipitates or each precipitate be examined as soon as produced; if the former method be adopted, confusion will be avoided by labelling or marking the funnels or papers holding the precipitate "the HCl ppt.," "the H_2S ppt.," and so on.

The colours and general appearance of the various sulphides and hydroxides precipitated should be borne in mind, as the absence of other substances, as well as the presence of those precipitated, is often at once thus indicated.

Application of confirmatory tests must be frequent.

Results of analyses should be recorded neatly in a memorandum book; *a*, for correction and endorsement by the teacher; *b*, for future reference by the student or by those who may need evidence respecting his labours; and, *c*, to promote mental orderliness.

The various reactions which occur in an analysis have already come before the reader in going through the tests for the individual metals or in other analytical operations; it is unnecessary, therefore, again to construct equations or diagrams. But the reactions should be thought over, and if not perfectly clear to the mind, be written out again and again, till thoroughly understood.

Special Memoranda.

The Hydrochloric-acid precipitate may at first include some antimony and bismuth as oxychlorides, readily dissolved, however, by excess of acid.——If either of these elements be present, the washings of the precipitate will probably be milky; in that case add a few drops of hydrochloric acid, which will clear the liquid and make way for the application of the test for lead.——The silver chloride and mercurous chloride precipitate should not be long in contact with the ammonia, or silver will be reprecipitated thus:—

$$2AgCl + 2HgCl + 4NH_3 = NHg_2Cl, NH_4Cl + 2NH_4Cl + 2Ag$$

The hydrogen sulphide precipitate may be whitish, in which case it is nothing but sulphur; for, as already indicated, ferric salts are reduced by hydrogen sulphide to ferrous, and chromates to chromic salts, finely divided whitish sulphur being deposited:—

$$4FeCl_3 + 2H_2S = 4FeCl_2 + 4HCl + S_2 ;$$
$$4CrO_3 + 2H_2S + 12HCl = 4CrCl_3 + 12H_2O + 3S_2$$

But the precipitate may also be very slightly yellow, or even white when only a mercuric salt is present, through an insufficiency of hydrogen sulphide having produced a chlorosulphide. The gas should be passed through the liquid until, even after well shaking, the latter smells strongly of hydrogen sulphide.

The portion of the hydrogen sulphide precipitate dissolved by ammonium hydrosulphide may include a trace of copper, cupric sulphide being not altogether insoluble in ammonium hydrosulphide.——On adding hydrochloric acid to the ammonium hydrosulphide solution, whitish or yellowish sulphur only may be precipitated, yellow ammonium hydrosulphide always containing free sulphur.——Concentrated hydrochloric acid does not readily dissolve small quantities of antimonious sulphide out of much arsenious sulphide; and, on the other hand, the concentrated hydrochloric acid takes into solution a small quantity of arsenious sulphide if much antimonious sulphide be present. The precipitates or the original solutions should therefore be examined by the other (hydrogen) tests for these elements if doubt exist concerning the presence or absence of either. Tin remains in the hydrogen-bottle in the metallic state, deposited as a black powder on the zinc used in the experiment. The contents of the bottle are turned out into a dish, ebullition continued until evolution of hydrogen ceases, and the zinc is taken up by the excess of sulphuric acid employed; any tin is then filtered out, washed, dissolved in a few drops of hydrochloric acid, and the liquid tested for tin by the usual reagents.——Tin may be detected in the mixed tin, arsenium, and antimony sulphides by the blowpipe reaction (p. 216).

The portion of the hydrogen sulphide precipitate not dissolved by ammonium hydrosulphide may leave a yellow semi-fused globule of sulphur on boiling with nitric acid. This globule may be black, not only from presence of mercuric sulphide, but also from enclosed particles of other sulphides protected by the sulphur from the action of the acid. It may also contain lead sulphate, produced by the action of nitric acid on lead sulphide. In cases of doubt the mass must be removed from the liquid, boiled with nitric acid till dissolved, the solution evaporated to remove excess of acid, and the residue examined; but usually it may be disregarded.——Before testing for bismuth, any considerable excess of acid should be removed by evaporation, and the residual liquid should be freely diluted. If no precipitate (bismuth oxynitrate) appear, ammonium chloride solution may be added, bismuth oxychloride more readily forming than even oxynitrate. Or, any nitric acid or sulphuric acid having been neutralized by adding ammonia, hydrochloric acid is added and then potassium iodide; a rich orange colour results if bismuth be present.——Bismuth may also be detected in the mixed precipitated bismuth and lead hydroxides, obtained in the ordinary course of analysis, by dissolving a portion of the precipitate in acetic acid, and adding the liquid to the hot solution of lead iodide mentioned in the reactions for bismuth (p. 260).——In testing for lead by means of sulphuric acid, the liquid should be diluted and set aside for some time.

Mercury may also be isolated by digesting the hydrogen sulphide precipitate in sodium hydrosulphide, instead of ammonium hydrosulphide. The arsenium, antimony, tin, and mercury sulphides are thus dissolved out. The mixture is then filtered, excess of hydrochloric acid added to the filtrate, and the precipitated sulphides collected on a filter, washed, and digested in ammonium hydrosulphide; mercury sulphide remains insoluble, while the arsenium, antimony, and tin sulphides are dissolved. By this method copper also appears in its right place only, cupric sulphide being insoluble in sodium hydrosulphide. The other metals are then separated in the usual way.

The ammonium hydrosulphide precipitate may, if the original solution was acid, contain barium-group and magnesium phosphates, oxalates, silicates, and borates. These will subsequently come out with the iron, and, being white, give the iron precipitate a light-coloured appearance; their examination must be conducted separately, by a method described subsequently in connection with the treatment of substances insoluble in water.——The precipitate containing aluminium, iron, and chromium hydroxides often contains some manganese. This manganese may be detected by washing the hydroxides to remove all trace of chlorides, boiling with nitric acid, adding either lead peroxide or red lead, and setting the vessel aside; if manganese be present, a red or purple liquid is produced.——Nickel sulphide is not easily removed by filtration (*see* p. 154) until most of the excess of ammonium hydrosulphide has been dissipated by prolonged ebullition.

The ammonium carbonate precipitate may not contain the whole of the barium, strontium, and calcium in the mixture, unless free ammonia be present; for the carbonates of these metals are soluble in water charged with carbonic acid. If, therefore, the liquid is not distinctly ammoniacal, solution of ammonia should be added.——Neither ammonium carbonate nor ammonia wholly precipitates magnesium salts; and as partial precipitation is undesirable, ammonium chloride, if not already present in the liquid, should be added.——In the Table opposite p. 276, it is directed that strontium be separated from calcium by adding dilute sulphuric acid to the acetic acid solution. This reagent, unless extremely dilute, may precipitate calcium. Any such loss of calcium is in itself of little consequence, because enough calcium sulphate remains in the filtrate to afford a calcium reaction when solution of ammonia and ammonium oxalate are subsequently added. But the calcium sulphate precipitated by the sulphuric acid may be wrongly set down as strontium sulphate. Therefore test a little of the acetic acid solution for strontium by adding an aqueous solution of calcium sulphate, when, if no precipitate falls after setting aside for several minutes, strontium may be regarded as absent. If a precipitate occurs, strontium is present: the rest of the acetic acid solution is then tested for calcium as directed in the Table, the final testing by means of ammonium oxalate being, of course, preceded by the addition of ammonia. —— Barium may be overlooked if oxidation happens to have converted any sulphur into sulphuric acid.

Lithium.—Should a precipitate, supposed to be due to lithium, be obtained, it must be tested in the Bunsen flame. If the characteristic crimson flame coloration is not observable, the precipitate is probably due to a small quantity of magnesium, which not infrequently shows itself under the conditions requisite for the precipitation of lithium. If present only in minute proportions, the lithium may also remain with the alkali-metals; it can then be detected by means of the spectroscope. Such a method of examination is called spectrum analysis, a subject of much interest and of no great difficulty; it will be described briefly in connection with the methods of analysing solid substances.

QUESTIONS AND EXERCISES

Describe a general method of analysis by which the metal of a single salt in a solution could be quickly detected.—Give illustrations of black, white, buff, yellow, and orange sulphides.—Mention the group-reagents usually employed in analysis.—Under what circumstances may a hydrochloric acid precipitate contain antimony or bismuth?—If a hydrogen sulphide precipitate is white, what substances are indicated?—Give processes for the qualitative analysis of liquids containing the following substances:—*a.* Arsenium and Cadmium. *b.* Bismuth and Antimony. *c.* Antimony and Mercurous salt. *d.* Silver and Mercurous salt. *e.* Ferrous and Ferric salts. *f.* Aluminium, Iron, and Chromium. *g.* Arsenium, Antimony, and Tin. *h.* Lead and Strontium. *i.* Lead and Mercuric salt. *j.* Copper and Arsenium. *k.* Aluminium and Zinc. *l.* Iron and Copper. *m.* Iron, Sodium, and Arsenium. *n.* Mercury, Manganese, and Magnesium. *o.* Zinc, Manganese, Nickel, and Cobalt. *p.* Barium, Strontium, and Calcium. *q.* Zinc, Magnesium, and Ammonium. *r.* Aluminium and Magnesium. *s.* Iron, Barium, and Potassium. *t.* Magnesium, Calcium, and Potassium. *u.* Silver, Antimony, Zinc, Barium, and Ammonium,

THE ACID RADICALS

With the exception of ammonium, NH_4, the twenty-seven radicals which have up to this point mainly occupied attention, are metals. They have been studied for the most part, not in the free or uncombined state, but in the condition in which they exist in salts, *i.e.*, as the metallic radicals of salts. As already mentioned (see p. 60), salts may be regarded as composed of a metallic radical united with an acid radical. Every acid, too, may be regarded as consisting of hydrogen, which plays the part of a metallic radical, united with an acid radical; and hence the acids are sometimes called hydrogen salts. When the place of this hydrogen in an acid is taken by a metal, the product is simply called a salt. In this section of the Manual, we shall take up the study of a number of important salts from the point of view of the acid radicals which they contain and, incidentally, we shall also study the acids, in which these radicals occur in combination with hydrogen.

Just as there are univalent, bivalent, etc., metallic radicals, so there are univalent, bivalent, etc., acid radicals. The acids corresponding to these radicals contain one, two, etc., atoms of displaceable hydrogen, and on this account are called monobasic, dibasic, etc., acids: thus, hydrochloric acid, HCl, is monobasic; sulphuric acid, H_2SO_4, is dibasic; orthophosphoric acid, H_3PO_4, is tribasic. Acids of higher basicity are also known.

The student should note carefully the signification of the words *strong* and *weak* as applied to acids, and must not confuse the ideas implied by these terms with those conveyed respectively by the description of acids as *concentrated* and *diluted* (not necessarily "diluted," *i.e.*, prepared by dilution). A strong acid is one which exhibits the characters of an acid in a well-marked manner, while a weak acid only possesses these characters to a limited extent. Considered in this respect, sulphuric acid is a strong acid, while acetic acid is a weak one. The *state of concentration* of an acid is often described as its "strength," but this usage is not to be commended, the single word "concentration" being the term which is now usually employed in chemistry to designate this degree of concentration or "state of concentration." Sulphuric acid, even when dilute, is still a strong acid, while acetic acid, even when highly concentrated, is still a comparatively weak acid. With regard to two samples of dilute acid, the one of which contains, say, fifteen, and the other twenty per cent. of sulphuric acid, it would be correct to say that the *concentration* of the latter is greater than that of the former, *i.e.*, that in any given volume of the latter solution there is more sulphuric acid than in the same volume of the former solution.

HYDROCHLORIC ACID, HCl, and other Chlorides

The acid radical of hydrochloric acid and of other chlorides is chlorine, Cl. Chlorine occurs in nature chiefly as sodium chloride, NaCl. Sodium chloride is a very abundant substance, occurring either solid as *rock-salt*, deposits of which exist in Cheshire, at Stassfurt, and elsewhere, or in solution in the water of all seas. Common table-salt is more or less pure sodium chloride in minute crystals. Chlorine, in hydrochloric acid and the chlorides, is univalent (Cl′); its atomic weight is 35·19. The molecular formula for chlorine is Cl_2. Hydrochloric acid is a monobasic acid.

Hydrochloric Acid

Experiment 1.—To a few fragments of sodium chloride in a test-tube or small flask, add about an equal weight of sulphuric acid; colourless hydrochloric acid gas is evolved, and sodium hydrogen sulphate remains. Adapt to the mouth of the vessel, by means of a perforated cork, a piece of glass tubing bent to a right angle; heat the mixture (fig. 10, p. 22, or fig. 37, below) and convey the gas into a little water; solution of hydrochloric acid results.

$$\underset{\text{Sodium chloride}}{NaCl} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Hydrochloric acid}}{HCl} + \underset{\text{Sodium hydrogen sulphate}}{NaHSO_4}$$

The product of this operation is the nearly colourless and very sour liquid commonly termed hydrochloric acid. When of certain "concentrations" (determined by volumetric analysis), it forms *Acidum Hydrochloricum*, B.P., and *Acidum Hydrochloricum Dilutum*, B.P. The former has a specific gravity of 1·16 (1·1578), and contains 31·79 per cent. of real acid; the latter, specific gravity 1·052, with 10·58 per cent. of real acid, is made by diluting 6 fluid parts of the more concentrated acid with water until the mixture measures 20 fluid parts. The above process is that of the manufacturer—larger vessels being employed, and the gas being freed from any trace of sulphuric acid by washing. Other chlorides yield hydrochloric acid when heated with sulphuric acid; but sodium chloride is always used because it is plentiful and therefore cheap.

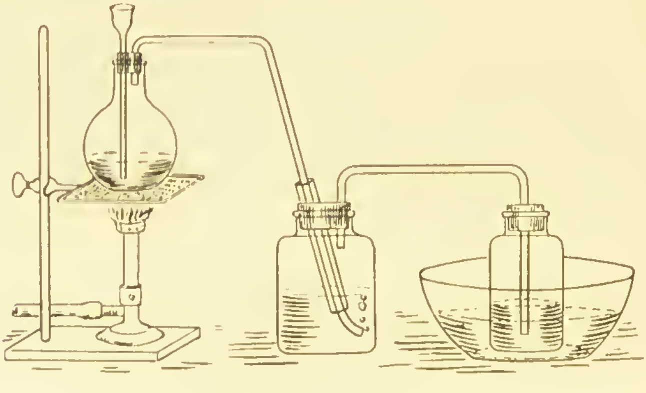

FIG. 37.—Preparation of Hydrochloric Acid.

Commercial hydrochloric acid is a by-product in the manufacture of sodium carbonate from common salt (by the process in which sodium chloride is first converted into sulphate, hydrochloric acid being liberated and dissolved in water). This impure acid has a yellow colour and is liable to contain iron, arsenium, alkali-metal salts, sulphuric acid, and nitrous compounds; sometimes, also, sulphurous acid or chlorine.

Invisible gaseous hydrochloric acid forms visible greyish-white fumes on coming into contact with air. This is due to its abstracting moisture from the air and dissolving in it, the fumes consisting of minute particles of solution of hydrochloric acid. The great readiness with which hydrochloric acid gas dissolves in water is strikingly demonstrated on opening a test-tube full of the gas under water; the latter rushes into and instantly fills the tube. If the water is tinged with blue litmus, the acid character of the gas is prettily shown at the same time. The test-tube, which should be perfectly dry, may be filled from the delivery-tube direct; for the gas is somewhat heavier than air and therefore readily displaces it. At low temperatures hydrochloric acid and water form a crystalline compound, $HCl, 2H_2O$.

Note.—The process, as described (p. 284), includes the use of as much sulphuric acid as is necessary for the production of the acid sodium sulphate, $NaHSO_4$, which remains in the generating vessel. A hot solution of this residue, neutralized by sodium carbonate, filtered and set aside, yields normal sodium sulphate (*Sodii Sulphas*, B.P.) Glauber's Salt, $Na_2SO_4,10H_2O$, in the form of transparent, oblique, efflorescent prisms.

$$\underset{\text{Sodium hydrogen sulphate}}{2NaHSO_4} + \underset{\text{Sodium carbonate}}{Na_2CO_3} = \underset{\text{Sodium sulphate}}{2Na_2SO_4} + \underset{\text{Water}}{H_2O} + \underset{\text{Carbonic anhydride}}{CO_2}$$

In the commercial preparation of sodium sulphate for the manufacture of sodium carbonate by the Leblanc process, the proportions in which the sodium chloride and the sulphuric acid are employed are those required to form normal sodium sulphate and not acid sodium sulphate. To carry out this reaction a higher temperature is necessary. $2NaCl + H_2SO_4 = 2HCl + Na_2SO_4$.

Chlorine

Experiment 2.—To some drops of hydrochloric acid (that is, the common aqueous solution of the gas) add a few grains of black manganese oxide, and warm the mixture; chlorine is evolved, and may be recognised by its peculiar odour, and by its highly irritating effect on the nose and air-passages.

$$4HCl + MnO_2 = Cl_2 + 2H_2O + MnCl_2$$

Chlorine-water.—The above is the process of the British Pharmacopœia for the production of chlorine-water (Solution of Chlorine, B.P.), the gas being first washed and then passed into water. One ounce of black manganese oxide to six fluid ounces of hydrochloric acid diluted with two of water (the resulting gas being passed through a wash-bottle containing about two ounces of water) yield enough chlorine to produce a pint and a half of chlorine-water. (On this small scale, less than half the acid is utilized, owing to incomplete decomposition of the materials and, especially, to incomplete absorption of the chlorine.) When chlorine-water is exposed to daylight, the chlorine slowly decomposes water with production of hydrochloric acid and oxygen; hence the solution should be freshly prepared; it is best preserved in a green glass well-stoppered bottle in a cool and dark place. At ordinary temperatures (60° F., 15·5° C.), if fresh and thoroughly saturated, chlorine-water contains more than twice (2·3 times) its bulk of chlorine, or less than 1 per cent. (about 0·75) by weight. Chlorine passed into cold water yields crystals of chlorine hydrate, $Cl_2,8H_2O$, and these, when heated in a sealed tube under pressure, give an upper layer of chlorine-water and a lower layer of *liquid chlorine.*

Note.—To obtain the chlorine from other chlorides, such as sodium chloride, sulphuric acid, as well as black manganese oxide, must be added. It may be assumed that hydrochloric acid is first formed by the action of sulphuric acid on the sodium chloride, and that this then interacts with black manganese oxide and more sulphuric acid to form chlorine, manganous sulphate, and water. The following equations may represent these steps in the process:—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl,$$
$$MnO_2 + 2HCl + H_2SO_4 = Cl_2 + MnSO_4 + 2H_2O;$$

or the whole may be included in one equation:

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$$

This reaction may occasionally have analytical interest, a very small quantity of a chloride being recognisable by its means. But the following reaction is nearly always applicable for the detection of this element, and leaves little to be desired in point of delicacy :—

Analytical Reaction of Chlorides.

To a drop of hydrochloric acid, or to a dilute solution of any other chloride, add solution of silver nitrate ; a white curdy precipitate of silver chloride, AgCl, is produced. Pour away the supernatant liquid, add nitric acid, and boil ; the precipitate does not dissolve. Pour away the acid, and add dilute solution of ammonia ; the precipitate quickly dissolves. Neutralize the solution by adding an acid ; the curdy precipitate again appears.

The formation of this white precipitate, its appearance, insolubility in boiling nitric acid, solubility in solution of ammonia and reprecipitation by an acid, form, in the known absence of bromide, abundant evidence of the presence of a chloride.

If free hydrochloric acid be present in quantity in a solution, it will, in addition to the reaction with silver nitrate, give rise to strong effervescence on the addition of a carbonate, a chloride being formed. The chlorine in insoluble chlorides, such as calomel, white precipitate, etc., may be detected by boiling with caustic alkali, filtering, acidulating the filtrate by means of nitric acid, and then adding the silver nitrate.

Antidotes.—In cases of poisoning by hydrochloric acid, solution of sodium carbonate (common washing-soda) or a mixture of magnesia and water may be administered.

QUESTIONS AND EXERCISES

The official Hydrochloric Acid contains 31·8 per cent. by weight of gas, and its specific gravity is 1·16 ; calculate what volume of it will be required, theoretically, to mix with black manganese oxide for the production of one gallon of chlorine-water, one fluid ounce of which contains 2·66 grains of chlorine. *Ans.*, $5\frac{1}{2}$ fl. ozs. nearly (5·4).—Why does hydrochloric acid gas give visible fumes on coming into contact with air?—How much sodium chloride will be required to furnish one pound of chlorine?—Give the analytical reactions of chlorides.—What antidotes may be administered in cases of poisoning by hydrochloric acid?

HYDROBROMIC ACID, HBr, and other Bromides

Bromine: Source, Preparation, and Properties.—The acid radical of hydrobromic acid and other bromides is bromine, Br (Bromine, B.P.). Bromine occurs in nature in the form of bromides in sea-water and certain saline springs, and is prepared from the *bittern*, or residual liquors of salt works. It may be liberated from bromides by a process similar to that employed for liberating chlorine from chlorides—that is, by heating with black manganese oxide and sulphuric acid (*see* note on p. 286); but is now largely obtained by liberating it from bromides by the action of chlorine. (Compare reaction 2, p. 290.) It is a dark-red volatile liquid of specific gravity, 2·97 to 3·14, and possessing an odour more irritating, if possible, than that of chlorine.—Its boiling point is 135-145° F., 57·2-62·7° C.). Bromine in hydrobromic acid and the bromides, is univalent (Br'). Its atomic weight is 79·35, and its molecular formula is Br_2.

Hydrobromic Acid.—Hydrogen bromide, or hydrobromic acid, may be made by decomposing phosphorus tri-bromide or pentabromide by means of water; $PBr_3 + 3H_2O = 3HBr + H_3PO_3$, or $PBr_5 + 4H_2O = 5HBr + H_3PO_4$. A small quantity is prepared by placing seven or eight drops of bromine at the bottom of a test-tube, putting in fragments of glass to the height of about an inch or two, then ten or eleven grains of red phosphorus, then another inch of glass, and finally a couple of inches of glass fragments slightly wetted with water, a delivery-tube being fitted by means of a cork. The phosphorus combines readily, almost violently, with the bromine as soon as the vapour of the latter, aided by gentle heating, comes into contact with the phosphorus. The phosphorus tri-bromide thus formed then suffers decomposition by the water of the moist glass, hydrobromic and phosphorous acids being produced. The hydrobromic acid gas passes over (further heat being applied in the later

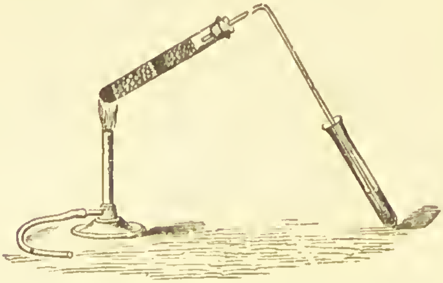

Fig. 38.—Preparation of Hydrobromic Acid.

stages of the operation) and may be led into water or solution of ammonia. The latter solution on evaporation yields ammonium bromide.

Solution of hydrobromic acid may also be prepared by passing hydrogen sulphide through bromine covered with water, until all colour has disappeared, and then distilling the mixture. $10Br_2 + 4H_2S + 8H_2O = 20HBr + 2H_2SO_4 + S_2$. A better method is that of Scott, who prepares pure solution of hydrobromic acid by passing purified sulphurous anhydride into water lying over a layer of bromine, until a homogeneous liquid, still slightly yellow from the presence of free bromine, is obtained; and then distilling this liquid several times, so as to remove uncombined bromine and traces of sulphuric acid. $Br_2 + SO_2 + 2H_2O = 2HBr + H_2SO_4$. For rapidly obtaining a solution of hydrobromic acid on a small scale, H. Marshall recommends the addition of sulphuric acid to a saturated solution of barium bromide, in a quantity nearly but not quite sufficient to precipitate the whole of the barium as sulphate, followed by filtration of the solution, and distillation.

Hydrobromic acid, like hydrochloric acid, is monobasic.

Acidum Hydrobromicum Dilutum, B.P., is prepared by the distillation of potassium bromide with concentrated phosphoric acid. Its specific gravity is 1·077, and it contains 10 per cent. by weight of hydrogen bromide, HBr.

Potassium Bromide, KBr, is very largely employed in pharmacy, and may be used in studying the reactions of bromides. The officially recognised method of making the salt has been alluded to under the potassium salts (p. 79).

Sodium Bromide crystallizes in anhydrous cubes, NaBr, from solutions at 110° to 120° F. (43·3°-48·8° C.), and in hydrous prisms, $NaBr, 2H_2O$, at ordinary temperatures.

Ammonium Bromide, NH_4Br (*Ammonii Bromidum*, B.P.), may be made by neutralizing hydrobromic acid with ammonia: $HBr + NH_4OH = NH_4Br + H_2O$. It forms colourless crystals which may become slightly yellow on exposure to air. It is readily soluble in water, less so in alcohol, and sublimes when heated.

Other bromides are seldom used; they may be prepared in the same way as the corresponding chlorides or iodides, which they closely resemble.

Solution of Bromine, B.P., 1 part in 150, is an aqueous solution, bromine being slightly soluble in water.

Hypobromites and *Bromates*, analogous to hypochlorites and chlorates, can easily be prepared.

Bromates, occurring as impurity in bromides, are detected by dropping dilute sulphuric acid upon the salt; a yellow colour, due to free bromine, is produced *immediately* if bromates are present:—

$$KBr + H_2SO_4 = HBr + KHSO_4$$
$$KBrO_3 + H_2SO_4 = HBrO_3 + KHSO_4$$
$$5HBr + HBrO_3 = 3Br_2 + 3H_2O$$

Analytical Reactions of Bromides.

1. To a few drops of a solution of a bromide (KBr or NH_4Br) add solution of silver nitrate; a yellowish-white precipitate of silver bromide, AgBr, is produced. Treat the precipitate successively with nitric acid and dilute solution of ammonia, as described under silver chloride; it is dissolved by the ammonia solution, but somewhat less readily than the silver chloride.

2. To a solution of a bromide add a few drops of chlorine water, or pass in some bubbles of chlorine gas; then add a few drops of chloroform, or ether, or carbon bisulphide, shake the mixture, and set the test-tube aside; the chlorine displaces the bromine, which is dissolved by the chloroform, ether, or carbon bisulphide (the solution falling to the bottom of the tube in the case of the heavy chloroform or carbon sulphide, or rising to the top in the case of the light ether). The solution of bromine has a distinct yellow, or reddish-yellow, or red colour, according to the amount of bromine present in it. $2KBr + Cl_2 = 2KCl + Br_2$.

Notes.—This reaction serves for the isolation of bromine when mixed with many other substances. Excess of chlorine must be avoided, as colourless bromine chloride is then formed. Iodides give a somewhat similar appearance; the absence of iodine must therefore be ensured by a process given in the next section. The above solution in chloroform or ether may be removed from the tube by drawing it up into a *pipette* (small pipe—a narrow glass tube, usually having a bulb or expanded portion in the middle); the bromine which it contains may be converted into relatively non-volatile salts by the addition of a drop of solution of caustic potash or soda; the chloroform or ether may then be removed by evaporation, and the residue tested as described in the next paragraph.

3. Liberate bromine from a bromide by the cautious addition of chlorine or chlorine-water, then add a few drops of cold mucilage of starch; a yellow combination of bromine and starch, termed "starch bromide," is formed.

Bromine may also be liberated from bromides by adding concentrated sulphuric acid and some black manganese oxide, and gently heating. Even sulphuric acid alone, if concentrated, liberates bromine from a bromide, the hydrogen of the hydrobromic acid combining to some extent with the oxygen of the sulphuric acid, and the latter being reduced to sulphurous anhydride:—

$$2KBr + 2H_2SO_4 = K_2SO_4 + Br_2 + SO_2 + 2H_2O$$

HYDRIODIC ACID, HI, and other Iodides

Iodine: Source.—The acid radical of hydriodic acid and other iodides is iodine, I. Iodine occurs in nature in the form of iodides, in sea-water. Sea-weeds, sponges, and other marine organisms, which derive much of their nourishment from sea-water, store up iodides in their tissues; and it is from the ashes of these that supplies of iodine (*Iodum*, B.P.) are obtained. Iodine also occurs in the form of iodates in crude sodium nitrate.

Preparation.—The sea-weed ash, or *kelp*, is treated with water, insoluble matter thrown away, and the decanted liquid evaporated and set aside to allow of the deposition of most of the sodium and potassium sulphates, carbonates, and chlorides. The residual liquor is treated with excess of sulphuric acid, which causes evolution of carbonic anhydride and of sulphurous anhydride or hydrogen sulphide, deposition of sulphur and more sodium sulphate, and formation of hydriodic acid. To the decanted liquid black manganese oxide is added, and the mixture is then slowly distilled; the iodine sublimes and is afterwards purified by resublimation.

$$2HI + MnO_2 + H_2SO_4 = MnSO_4 + 2H_2O + I_2$$

Properties.—Iodine is a crystalline purplish-black solid; its vapour, readily seen on heating a fragment in a test-tube, is dark violet. The vapour is irritating to the lungs; but a trace may be inhaled with safety. Iodine melts at 230° F. (110° C.), boils at about 392° F. (200° C.), the first portions containing any cyanogen iodide that may be present. The latter substance, which is rarely present in iodine, forms slender, colourless prisms, which emit a pungent odour.

Solution of Iodine.—Iodine is slightly soluble in water (iodine-water), and readily soluble in an aqueous solution of potassium iodide.* One and a quarter ounces of iodine and three-quarters of an ounce of potassium iodide, dissolved in a mixture of distilled water and alcohol, form *Liquor Iodi Fortis*, B.P. *Tinctura Iodi*, B.P., is a similar preparation of different strength. 20 grains of iodine and 20 of potassium iodide, rubbed with 60 grains of glycerin, and 400 grains of lard, form *Unguentum Iodi*, B.P.

Iodine combines with sulphur, forming an unstable, greyish-black, solid iodide, S_2I_2, having a radiated crystalline structure (*Sulphuris Iodidum*, B.P.). *Unguentum Sulphuris Iodidi*, B.P., is a mixture of this iodide with glycerin and lard.

Iodine, in hydriodic acid and the iodides, is univalent (I'). The atomic weight of iodine is 125·9; its molecular formula is I_2.

Hydriodic Acid.—Hydrogen iodide, or hydriodic acid, is a heavy colourless gas. A solution of it in water may be made by passing hydrogen sulphide into water in which iodine is suspended, the chief reaction being:—$H_2S + I_2 = S + 2HI$. *See* the analogous reaction for HBr, p. 289.

Hydriodic acid may also be prepared by placing twenty parts of iodine and two of water in a retort, the neck of which points upwards and the end of the neck of which is connected by a glass tube with a bottle or other vessel containing a little water. Into the tubulure of the retort there is passed (at first a drop at a time) a mixture of one part of red phosphorus with two of water. Abundance of hydriodic acid is evolved on the gentle application of heat, and dissolves in the water in the receiver. Phosphoric acid remains.—

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* Iodine forms differently coloured solutions with different solvents; *e.g.* the solution in water, alcohol, ether, or aqueous solution of potassium iodide is brown, while the solution in chloroform, benzene, or carbon bisulphide, is violet.

$P_4 + 10I_2 + 16H_2O = 20HI + 4H_3PO_4$. *See* the analogous reaction for HBr, p. 288.

Hydriodic acid may also be prepared by dissolving iodine in carbon bisulphide in a tall cylinder, adding water and passing hydrogen sulphide through the mixture. The water dissolves the hydriodic acid produced, the bisulphide retaining the sulphur. The aqueous solution only needs boiling for two or three minutes to remove excess of hydrogen sulphide.

Syrupus Acidi Hydriodici, U.S.P., contains about 1 per cent. of hydrogen iodide.

Potassium Iodide, KI, is largely used in medicine, and is a convenient salt on which to experiment in studying the reactions of iodides.

Nitrogen Iodide is formed when excess of aqueous ammonia is added to a solution of iodine in potassium iodide.

Analytical Reactions of Iodides.

1. To a few drops of an aqueous solution of an iodide (*e.g.* KI) add solution of silver nitrate; a pale yellow precipitate of silver iodide, AgI, is produced. Pour away the supernatant liquid, and treat the precipitate with nitric acid; it is not dissolved. Pour away the acid, and then add solution of ammonia; the precipitate is almost unchanged.

2. Liberate iodine from an iodide by the cautious addition of chlorine-water, then add starch mucilage; a deep-blue combination of iodine and starch, termed "starch iodide," is formed.

This reaction is very delicate and characteristic. Heat decomposes the blue compound. Excess of chlorine must be avoided, or a solution of iodic acid will be produced, which is colourless. Nitrous acid, or a nitrite acidulated with sulphuric acid, may be used instead of chlorine. Concentrated sulphuric acid also liberates iodine from iodides, the hydrogen of the hydriodic acid first produced uniting with the oxygen of the sulphuric acid whereby the latter is reduced to sulphurous anhydride, or even to hydrogen sulphide.

In testing bromine for the presence of iodine, the bromine must be nearly all converted into hydrobromic acid by means of dilute solution of sulphurous acid (*see* p. 289, Scott's process) or be nearly all removed by addition of caustic soda, before the starch mucilage is added.

Ozone (O_3).—Papers soaked in starch mucilage containing potassium iodide form a test for free chlorine and nitrous acid, and are also employed by meteorologists to detect an allotropic and very active form of oxygen, termed by Schönbein *ozone* (from ὄζω, *ozō*, I smell), which also liberates iodine from potassium iodide with formation of starch iodide. Ozone is supposed to occur normally in the atmosphere, the salubrity or insalubrity of which is said to be dependent to some extent on its presence or absence. The possible occurrence in the air of nitrous or other oxidizing gases (as well as ozone) renders the starch test untrustworthy. Houzeau proposed to test for ozone by exposing litmus-paper of a neutral tint soaked in a dilute solution of potassium iodide: the alkali set free by the action of the ozone turns the paper blue. The same paper without iodide would indicate the extent to which the effect might be due to ammonia. Ozone, or rather, ozonized air, is produced artificially in large quantities by passing air through a box (Beane's Ozone generator) in which it is exposed to the silent electrical discharge. In the latter operation condensation of the volume of air, or rather, of the oxygen in the air, occurs. Ozone is also produced in small quantity when phosphorus undergoes slow oxidation in moist air, some hydrogen peroxide and ammonium nitrate being formed at the same time. Ozone is a powerful bleaching, disinfecting, and oxidizing agent; it is very sparingly soluble in water, but soluble in oils of turpentine and cinnamon, and in some other liquids. Its odour is characteristic. From experiments that have been made by Soret on the specific gravity of ozone, its molecular formula seems to be O_3, that of ordinary oxygen being O_2.

3. To a neutral aqueous solution of an iodide add a solution containing one part of cupric sulphate and two and a half parts of ferrous sulphate, and well shake; a dirty-white precipitate of cuprous iodide, CuI, is produced.

$$2KI + 2CuSO_4 + 2FeSO_4 = 2CuI + K_2SO_4 + Fe_2(SO_4)_3$$

Or to the liquid containing an iodide add solution of cupric sulphate and some solution of sulphurous acid, and warm the mixture; cuprous iodide is again produced.

$$2KI + 2CuSO_4 + H_2SO_3 + H_2O = 2CuI + 2KHSO_4 + H_2SO_4$$

Separation of Chlorides, Bromides, and Iodides.—Chlorides and bromides are not precipitated by cupric sulphate; the above reaction is useful, therefore, in removing iodine from a solution in which chlorides and bromides may also be present. The total removal of iodine by the former of the two modifications of the process is ensured by following up the addition of the cupric and ferrous sulphates by adding a few drops of solution of potassium or sodium hydroxide, any acid which might retain cuprous iodide in solution being thereby neutralized; ferric or ferrous hydroxide, precipitated at the same time, not affecting the reaction. Occasionally, too, it may be necessary to repeat the process with the filtrate before the last traces of iodine are removed. The second modification of the process is, on the whole, to be preferred.

Hart's Test.—(If nitrates, chlorates, bromates, or iodates are present, it is necessary to fuse the substance with a little sodium carbonate and charcoal to reduce them. If the chlorine, bromine, and iodine, are united with silver, it is best to fuse with sodium carbonate and extract with water, although with iodine and bromine this is not absolutely necessary.) The substance is placed in the flask shown in the figure given in the section on the quantitative analysis of manganese oxide (*see* Index), with some water and a few drops of solution of ferric sulphate. Into the bulbs a few drops of dilute starch mucilage are poured. The bulbs are kept cold by immersing in water in a beaker. The contents of the flask are then boiled, and if iodine is present the starch is coloured blue. This test is extremely delicate. If iodine is found, the cork and the bulb tube are removed, and the solution boiled until, on testing again in the same way, no more iodine is found. If much iodine is present, it is necessary to add more ferric sulphate solution. The bulb tube is now cleaned, charged with a few drops of water and a drop or two of chloroform, and a very small crystal of potassium permanganate is added to the solution in the flask. The contents of the flask are boiled again, and if bromine is present the chloroform becomes red. The tube is now removed, and more potassium permanganate and ferric sulphate added little by little, the mixture being boiled between each addition until the bromine has all been driven off. A few drops of alcohol are added to the contents of the flask to decolorize any excess of permanganate, and, after filtration, chlorine is tested for in the filtrate by means of silver nitrate.

Detection of Chloride in presence of Bromide or Iodide or both.—To a small quantity of the mixed solution add excess of silver nitrate in presence of nitric acid, and wash the precipitate once or twice with water by decantation. Then pour upon the precipitate 1 c.c. of a very dilute solution of potassium iodide (1 part in 1000 of water), add a few drops of dilute nitric acid, allow to stand in the cold for an hour with occasional shaking, and filter. Divide the filtrate into two parts, and add silver nitrate to one part and a drop of diluted chlorine water to the other. If the silver nitrate produces a *white* precipitate* and the chlorine does not liberate either bromine or iodine, then the original precipitate contained silver chloride.

The action of the potassium iodide on the silver chloride is represented by the equation:—$AgCl + KI = AgI + KCl$. If there is enough silver chloride present in the original precipitate, all the added potassium iodide is converted into potassium chloride and it is the latter which gives the white precipitate on the addition of silver nitrate. If the chlorine water liberates bromine or iodine, this shows (when not more than 1 c.c. of the 1 in 1000 potassium iodide has been used) that distinctly less than 1 milligramme of silver chloride, *and probably none at all*, was present.

Chlorides may also be detected in presence of bromides and iodides by taking advantage of the formation of chlorochromic anhydride (p. 185) and the non-occurrence of corresponding compounds of bromine or iodine, as follows:—

To a solution of a mixture of an iodide with a bromide and a chloride add a concentrated solution of sodium sulphite, then a reagent prepared by mixing equal volumes of sulphuric acid and saturated solution of cupric sulphate, until no further precipitation of cuprous iodide occurs. Next add solution of sodium hydroxide to remove the excess of copper, filter, and evaporate to dryness. Transfer the dried residue, together with an equal bulk of potassium bichromate, to a dry test-tube fitted with a delivery-tube, or to a small retort, and cover the mixture with sulphuric acid. Distil into water. Chromic anhydride and hydrochloric and hydrobromic acids are liberated by the sulphuric acid, and interacting with one another, form chlorochromic anhydride, together with free bromine and chlorine.

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* Silver nitrate produces a precipitate in any case, which may consist of silver chloride, bromide, or iodide and may, therefore, be pure white, yellowish, or yellow.

$$CrO_3 + 2HCl = CrO_2Cl_2 + H_2O$$
$$2CrO_3 + 6HBr + 3H_2SO_4 = Cr_2(SO_4)_3 + 3Br_2 + 6H_2O$$
$$2CrO_3 + 6HCl + 3H_2SO_4 = Cr_2(SO_4)_3 + 3Cl_2 + 6H_2O$$

The chlorochromic anhydride is decomposed by the excess of water into which it distils, giving rise to anhydrochromic acid, which imparts its orange colour to the liquid, and hydrochloric acid, thus: $2CrO_2Cl_2 + 3H_2O = H_2Cr_2O_7 + 4HCl$. The chlorine which is produced in the reaction escapes, and the bromine is dissolved by the water. The coloured liquid is then shaken with chloroform, which removes the bromine, indicating bromides in the original substance; a yellow or orange colour remaining is due to anhydrochromic acid, indicating chlorides in the original substance. Or ammonia may be added to the distillate; the colour due to bromine is thereby entirely removed, while the yellow colour of ammonium chromate remains.

Instead of eliminating the iodine as cuprous iodide, it may be expelled in vapour (obvious enough by its colour and odour) by fusing the dry mixture of the salts with excess of powdered potassium bichromate. The residue, broken into small fragments, may then be distilled with sulphuric acid for the detection of the bromine and chlorine.

$$5K_2Cr_2O_7 + 6KI = 8K_2CrO_4 + Cr_2O_3 + 3I_2$$

4. Iodides have been shown to be useful in testing for mercuric salts (*see* the Mercury reactions, p. 244); a mercuric salt (corrosive sublimate, for example) may therefore be used in testing for iodides, a scarlet precipitate of mercuric iodide, HgI_2, being produced.

This reaction may be employed where comparatively large quantities of an iodide are present; but its usefulness in analysis is limited by the fact that the precipitate is soluble in excess of the dissolved iodide, or in excess of the mercuric solution. The colour of the precipitate and its insolubility in water distinguish it from mercuric chloride, bromide, and cyanide, which are white soluble salts.

5. Iodides have also been shown to be useful in testing for lead salts (*see* the Lead reactions, p. 252); similarly a lead salt (acetate, for example) may be used in testing for iodides in solutions which are either neutral or faintly acid with acetic acid, a yellow precipitate of lead iodide, PbI_2, soluble in hot water and crystallizing in yellow scales on cooling, being produced.

Lead chloride, bromide, and cyanide are white; hence the above reaction may occasionally be useful in distinguishing iodides from chlorides, bromides, or cyanides. But lead iodide is slightly soluble in cold water; hence small quantities of iodides cannot be detected by means of this reaction. (For Iodates, *see* p. 317.)

Analogies between Chlorine, Bromine, Iodine and their Compounds.—These elements form a natural group or family, the members of which are closely related and exhibit a distinct gradation in physical properties. Thus chlorine is a gas and iodine a solid, while bromine occupies the intermediate liquid condition. The atomic weight of bromine is nearly midway between those of chlorine and iodine. The specific gravity of liquid chlorine is 1·33, of iodine 4·95, while that of bromine is nearly 3. Liquid chlorine is transparent, iodine opaque, bromine intermediate. The crystalline forms of the chloride, bromide, and iodide of the same metal are commonly identical. One volume of either element in the gaseous state combines with an equal volume of hydrogen (at the same temperature and pressure) to form two volumes of a gaseous acid, very soluble in water (hydrochloric acid, hydrobromic acid, hydriodic acid). By their union with metals, chlorine, bromine, and iodine form salts, of which sodium chloride, bromide, and iodide may be taken as types. On this account they have been called the *halogens* (*i.e.* salt producers), and the salts are called *haloid salts* (from ἅλς, *hals*, sea-salt, and εἶδος, *eidos*, likeness).

QUESTIÔNS AND EXERCISES

State the method by which bromine is obtained from its natural compounds.—Mention the properties of bromine.—How may potassium and ammonium bromides be made?—By what reagents may bromides be distinguished from chlorides?—Whence is iodine obtained?—By what process is iodine isolated?—State the properties of iodine.—What is the nature of sulphur iodide?—Give the analytical reactions of iodides.—What three substances may, indirectly, be detected by a mixture of potassium iodide and starch mucilage?—Describe two methods by which iodides may be removed from a solution containing chlorides and bromides.

HYDROCYANIC ACID, HCN, and other Cyanides

The acid radical of hydrocyanic acid and other cyanides is a compound group, the cyanogen radical, CN (or shortly, Cy). It is so named from κύανος, *kuanos*, blue, and γεννάω, *gennao*, I generate, in allusion to its prominent chemical character of forming, with certain iron compounds, the different varieties of Prussian blue. It was from Prussian blue that Scheele, in 1782, first obtained what we now, from our knowledge of its composition, call hydrocyanic acid, HCN or HCy, also called prussic acid. Cyanogen, C_2N_2, was isolated by Gay-Lussac in 1814, and was the first compound radical distinctly proved to exist.

Sources, etc.—Certain compounds containing the cyanogen radical occur in nature, and others can easily be prepared. Ammonium cyanide is found in small quantities among the gases of iron furnaces, and is produced to a slight extent in distilling coal for gas. In the preparation of potassium ferrocyanide the cyanogen radical is formed abundantly by heating animal refuse containing nitrogen, such as the scrapings of horns, hoofs, and hides (5 parts), with crude potassium carbonate (2 parts) and waste iron (filings, etc.) in a covered iron pot. The residual mass, which contains potassium cyanide, but no ferrocyanide, is boiled with water, the mixture filtered, and the filtrate evaporated and set aside for crystals of ferrocyanide to form. The cyanogen, produced from the carbon and nitrogen of the animal matter, unites with the potassium to form potassium cyanide and this afterwards, on boiling with water, interacts with iron sulphides (produced by the interaction of the iron with sulphur occurring in the nitrogenous organic matters, and as sulphate in the crude potassium carbonate) to form what is often termed yellow prussiate of potash, Potassium Ferrocyanide, B.P., $K_4FeC_6N_6,3H_2O$, a compound occurring in four-sided tabular yellow crystals. This salt contains the elements of cyanogen; yet is not a cyanide, but a ferrocyanide. It is not poisonous, and is otherwise different from cyanides; it will be further noticed subsequently. From this salt all cyanides are directly or indirectly prepared.

Potassium cyanide, KCN or KCy, the commonest cyanide, may be obtained by heating potassium ferrocyanide to redness until gas (chiefly nitrogen) is no longer evolved and iron carbide settles to the bottom of the molten mass of almost pure cyanide. The product, carefully poured off and cooled, is an opaque crystalline mass containing about 95 per cent. of potassium cyanide. It may also be produced by fusing eight parts of potassium ferrocyanide with three of potassium carbonate in a crucible; carbonic anhydride is evolved, iron is set free, and potassium cyanate, KCNO (*see* p. 370), is formed, as well as potassium cyanide:—

$$K_4FeC_6N_6 + K_2CO_3 = 5KCN + KCNO + Fe + CO_2$$

Mercuric cyanide is produced in crystals by dissolving 1 part of potassium ferrocyanide in 15 parts of boiling water, adding 2 parts of mercuric sulphate, keeping the whole hot for ten to fifteen minutes, and then filtering and setting aside to cool. Besides mercuric cyanide, $Hg(CN)_2$, ferric sulphate and potassium sulphate are formed, and mercury is set free. Any excess of ferrocyanide gives Prussian blue by interaction with the ferric sulphate.

Mercuric cyanide is exceptional in some of its analytical reactions, both as a mercuric salt and as a cyanide. Thus its solution does not give any precipitate with potassium iodide (*see* reaction 1 of Mercuric Salts, p. 244) unless a drop of hydrochloric acid has previously been added; neither does it yield the usual yellow and white precipitates with caustic potash and with ammonia respectively. Similarly it does not give the silver nitrate reaction for cyanides (*see* reaction 1, p. 302).

Cyanogen, C_2N_2, may be isolated by heating mercuric cyanide, $Hg(CN)_2$, or silver cyanide, AgCN. A small flame of cyanogen may be obtained by heating a few crystals of mercuric cyanide in a short piece of glass tubing closed at one end, and applying a light to the other end as soon as evolution of gas commences: brown *paracyanogen*, $(CN)_m$, and mercury are also produced. In the case of silver cyanide metallic silver remains. Cyanogen is a colourless gas which burns with a beautiful peach-blossom coloured flame.

Diluted Hydrocyanic Acid

Experiment.—Dissolve 2 or 3 grains of potassium ferrocyanide in 5 or 6 times its weight of water in a test-tube, add a few drops of sulphuric acid and boil the mixture, conveying the evolved gas through a bent glass tube (adapted to the test-tube by means of a cork) into another test-tube containing a little water; the product is a dilute solution of hydrocyanic acid. Made by this process in larger quantities and of a certain definite strength, this solution is the *Acidum Hydrocyanicum Dilutum*, B.P. It is a colourless liquid with a characteristic odour and is exceedingly poisonous. Sp. gr. 0·997. It contains 2 per cent. by weight of hydrogen cyanide, HCN.

$$2K_4FeC_6N_6 + 6H_2SO_4 = FeK_2FeC_6N_6 + 6KHSO_4 + 6HCN$$

To prepare a larger quantity proceed as follows, carrying out the operation in a well ventilated fume-cupboard:—Dissolve $2\frac{1}{4}$ ounces of potassium ferrocyanide in 10 ounces of water, add one fluid ounce of sulphuric acid previously diluted with 4 ounces of water and cooled. Put the solution into a flask or other suitable apparatus of glass or earthenware, to which are attached a condenser and a receiver arranged for distillation (*see* p. 138); and having put 8 ounces of distilled water into the receiver, and provided efficient means for keeping the condenser and receiver cold, apply heat to the flask, until by slow distillation the liquid in the receiver is increased to 17 fluid ounces.* Add to this 3 ounces of distilled water, or as much as may be sufficient to bring the acid to the required concentration. The end of the condenser, or an attached tube, should pass quite into the receiver.

The residue from this reaction is acid potassium sulphate,

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* This operation is peculiarly liable to those sudden and tumultuous evolutions of vapour, or "bumpings," which often interfere with successful distillation. Such bumping may usually be prevented and quiet ebullition ensured by placing in the liquid, before beginning to heat it, a few small fragments of unglazed earthenware, such as tobacco-pipe stem.

$KHSO_4$, which remains in solution, and potassium ferrous ferrocyanide, $FeK_2FeC_6N_6$, an insoluble powder sometimes termed Everitt's salt, from the name of the chemist who first made out the nature of the interaction. The latter compound becomes bluish green during the operation, owing to absorption of oxygen.

Pure anhydrous hydrocyanic acid is a colourless, highly volatile, intensely poisonous liquid, solidifying when cooled to a low temperature. It may be made by passing hydrogen sulphide over mercuric cyanide. The official solution of the acid is moderately stable, but is said to be rendered more so by the presence of a minute trace of sulphuric or hydrochloric acid. A more concentrated acid is liable to take up the elements of water and yield ammonium formate, NH_4CHO_2. Solutions of hydrocyanic acid often become brown by formation of what is, apparently, *paracyanogen*, $(CN)_n$. According to Williams, aqueous hydrocyanic acid containing 20 per cent. of glycerin can be kept for an almost indefinite length of time. The official acid should be preserved in well-stoppered bottles tied over with impervious tissue and kept inverted, when not in use, in a cool dark place. Unless such precautions are adopted, the solution rapidly becomes less concentrated by escape of gaseous hydrocyanic acid.

Hydrocyanic acid also occurs in cherry-laurel water and bitter-almond water.* *Aqua Laurocerasi*, B.P., is made to contain 0·1 per cent. of hydrocyanic acid, HCN.

The methods of determining the concentration of hydrocyanic acid solutions will be given in the chapter on volumetric and gravimetric quantitative analysis. The volumetric method is based on the formation of silver cyanide and its solubility in solution of alkali-metal cyanides, as described in reaction 1, below. The hydrocyanic acid used in pharmacy is extremely liable to variation in strength. It should frequently be tested volumetrically.

Analytical Reactions of Cyanides.

1. To a few drops of the hydrocyanic acid solution produced in the foregoing experiment, or to a solution of any cyanide (except mercuric cyanide), add excess of solution of

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* Traces are formed when an electric current passes between carbon poles in slightly moist air (Dewar); also during the action of nitric or nitrous acid on sugar, caramel, or finely divided charcoal.

silver nitrate; a white precipitate of silver cyanide, $AgCN$, is produced. When the precipitate has subsided, pour away the supernatant liquid and place half of the residue in another test-tube: to one portion add nitric acid, and notice that the precipitate does not dissolve; to the other add ammonia, and observe that the precipitate, though soluble, dissolves somewhat slowly. (Silver chloride, which is also white, is readily soluble in ammonia.) Silver cyanide dissolves in solutions of cyanides of alkali-metals, soluble double cyanides being formed (*e.g.*, $KCN,AgCN$, or $KAg(CN)_2$). Silver cyanide also dissolves in hot concentrated nitric acid.

Solubility of precipitates in concentrated solutions of salts.—Silver cyanide and many other precipitates insoluble in acids (or in alkalies) are often soluble in the saline liquids formed by the addition of acids and alkalies to each other. Hence the precaution of adding the latter reagents to separate portions of a precipitate when examining its solubility, or of not adding the one until the other has been poured away.

Hydrocyanic acid and other cyanides may be detected in the presence of potassium ferrocyanide by distilling with a large excess of sodium bicarbonate and testing the distillate for hydrocyanic acid. In the case of mercuric cyanide it is necessary to add a little hydrogen sulphide.

2. To a dilute solution of hydrocyanic acid, or of a soluble cyanide (except mercuric cyanide), add a few drops each of solutions of a ferrous and of a ferric salt (ferrous sulphate and ferric chloride); to the mixture add caustic potash or soda, magnesia, or sodium carbonate, and then excess of hydrochloric acid; a precipitate of Prussian blue remains. The decompositions may be traced in the following equations:—

$$\begin{aligned}
HCN &+ KOH &= KCN &+ H_2O \\
2KCN &+ FeSO_4 &= FeC_2N_2 &+ K_2SO_4 \\
4KCN &+ FeC_2N_2 &= K_4FeC_6N_6 & \\
3K_4FeC_6N_6 &+ 4FeCl_3 &= 12KCl &+ Fe_4(FeC_6N_6)_3
\end{aligned}$$

The test depends on the conversion of the cyanogen radical of the cyanide into ferrocyanogen by aid of the iron of a ferrous salt, and the combination of the ferrocyanogen, so produced, with the iron of a ferric salt.

3. To a solution of hydrocyanic acid add ammonia and yellow ammonium hydrosulphide, and evaporate the liquid nearly or quite to dryness in a small dish, occasionally adding ammonia till the excess of ammonium hydrosulphide is decomposed; add water and acidulate the liquid with hydrochloric acid, and then add a drop of solution of a ferric salt; a blood-red solution of ferric thiocyanate will be formed.

This is a very delicate reaction. Some free sulphur in the yellow ammonium hydrosulphide unites with the alkali-metal cyanide and forms thiocyanate ($NH_4CN + S = NH_4SCN$). If the liquid has not been evaporated far enough, ammonium hydrosulphide may still be present, and give black ferrous sulphide on the addition of the ferric salt, hence the acidulation prior to the addition of the ferric salt.

Hydrocyanic acid in the blood.—According to Buchner, the blood of animals poisoned by hydrocyanic acid, instead of coagulating as usual, remains liquid and of a clear cherry-red colour for several days. In one case he obtained the reactions of the acid on diluting and distilling the blood fifteen days after death, and applying the usual reagents to the distillate. Aqueous solution of hydrogen peroxide changes such blood to a deep-brown colour.

Schönbein's test for hydrocyanic acid is said to be extremely delicate. Filter-paper is soaked in a solution of 3 parts of guaiacum resin in 100 of alcohol. A strip of this paper is dipped in a solution of 1 part of cupric sulphate in 50 of water; a little of the suspected solution is placed on this paper and exposed to the air; the paper immediately turns blue if hydrocyanic acid be present. Or the paper may be placed over the mouth of an open bottle of medicine supposed to contain hydrocyanic acid, or may be otherwise exposed to the vapour of a suspected liquid.

Antidote

A mixture of ferrous sulphate, solution of ferric chloride, and either magnesia or sodium carbonate is the recognised *antidote* in cases of poisoning by hydrocyanic acid or potassium cyanide. In such an alkaline mixture the poisonous cyanide, by interaction with ferrous hydroxide, is at once converted into innocuous potassium or other ferrocyanide: should the mixture become acid, the ferric salt present interacts with the soluble ferrocyanide, forming insoluble Prussian blue which is also inert. From the rapidity of the action of these poisons, however, there is seldom time to prepare an antidote. Emetics, the stomach-pump, or stomach-siphon, the application of a stream of cold water to the spine, and the above antidote, form the usual treatment.

QUESTIONS AND EXERCISES

Write a paragraph on the discovery of hydrocyanic acid and of cyanogen.—Mention the source of the cyanogen of cyanides.—How is potassium ferrocyanide prepared?—What is the formula of potassium ferrocyanide?—Is potassium ferrocyanide poisonous?—Write an equation expressive of the reaction which ensues when potassium ferrocyanide and carbonate are brought together at a high temperature.—What are the properties of cyanogen? How may it be obtained in a pure condition?—How is mercuric cyanide prepared? What other substances and secondary products are formed at the same time?—How much hydrocyanic acid is contained in the official *Acidum Hydrocyanicum Dilutum?*—Give details of the preparation of hydrocyanic acid, and an equation representing the reaction.—State the proportion of water that must be added to an aqueous solution containing 15 per cent. of hydrocyanic acid to reduce the strength to 2 per cent. *Ans.*, $6\frac{1}{2}$ to 1.—What are the characters of pure undiluted hydrocyanic acid? How may it be obtained?—Enumerate the tests for cyanides, giving equations.—Explain the action of the best antidote in cases of poisoning by hydrocyanic acid or potassium cyanide. Show how it acts in alkaline and acid solutions respectively.

NITRIC ACID, HNO_3, and other Nitrates

Sources.—Nitrogen peroxide, N_2O_4, is formed to some extent in the atmosphere by the combination of nitrogen and oxygen under the influence of the powerful electrical discharges during thunderstorms. This oxide undergoes further oxidation in presence of water; and with ammonia, which is always a constituent of the atmosphere, it forms ammonium nitrate. The nitrates found in rain no doubt originate partly or wholly in this manner. The oxidation of ammonia and of the nitrogenous constituents of animal and vegetable matters in the soil, favoured by darkness, by the presence of calcium carbonate, and especially by the presence of the nitrifying organisms, results in the production of nitrates. Hence nitrates are commonly met with in natural waters, and in soils and the juices of plants. In the concentrated plant juices, termed medicinal "Extracts," small prismatic crystals of potassium nitrate may occasionally be observed. (The cubical crystals often met with in extracts are potassium chloride.) Nitric acid and other nitrates are prepared from potassium and sodium nitrates, which, in turn are obtained from the surface layers of the soil of tropical countries. *Potassium nitrate* (or *prismatic nitre,* from the form of its crystals), is produced in and about the villages of India. The natives simply scrape the surface of waste grounds, mud-heaps, banks, and other spots where a slight incrustation indicates the presence of appreciable quantities of nitre, mix the scrapings with wood-ashes, containing potassium carbonate (to decompose the calcium nitrate always present), digest the mixture in water, and evaporate the liquor. The immediate product is purified by careful recrystallizations, and is sent into commerce in the form of white crystalline masses or fragments of striated six-sided prisms (*Potassii Nitras,* B.P.). Besides its use in medicine, it is employed in very large quantities in the manufacture of gunpowder. *Charta Potassii Nitratis,* U.S.P., is prepared by soaking white filter-paper in a 20 per cent. solution of nitre, and drying. Potassium nitrate is also largely prepared by the interaction of potassium chloride and sodium nitrate. *Sodium nitrate* occurs in deposits from 3 inches to 3 yards in thickness on and near the surface, and at any depth down to about 30 feet, in many parts of Peru, Bolivia, and Chili, but more especially in the district of Atacama. The mineral is termed *caliche,* and commonly contains 50 per cent. of sodium nitrate. The latter is distinguished as *Chili saltpetre* or *Chili nitre,* or (from the form of its crystals — obtuse rhombohedra, not cubes) *cubic nitre,* and is chiefly used as a fertilizer and as a source of nitric acid, its tendency to absorb moisture unfitting it for use in gunpowder. In some parts of Europe potassium nitrate is made artificially by exposing heaps of animal manure, refuse, ashes, and soil to the action of the air and the heat of the sun; in the course of a year or two the nitrogen of the animal matter becomes oxidized to nitrates; the latter are removed by washing. According to Warington, the nitrifying ferment appears capable of existing in three conditions: (1) The nitric ferment of soil, which converts both ammonium salts and nitrites into nitrates; (2)

the altered ferment, which converts ammonium salts into nitrites, but fails to change nitrites into nitrates; and (3) the surface organism (a bacterium), which changes nitrites into nitrates. Similar nitrification goes on in well and river waters containing nitrogenous organic contaminations such as sewage, which thereby tend to become less noxious.

Note.—The word *nitric* is from *nitre,* the English equivalent of the Greek *νίτρον* (*nitron*), a name applied to certain natural deposits of *natron* (sodium carbonate) for which potassium nitrate seems at first to have been mistaken. *Saltpetre* is simply *sal petræ,* salt of the rock, in allusion to the natural origin of potassium nitrate. *Sal prunella* (from *sal,* a salt, and *pruna,* a live coal) is potassium nitrate melted over a fire and cast into cakes or bullets.

The nitric radical is univalent (NO_3').

Nitric Acid

Experiment. — To a fragment of potassium or sodium nitrate in a test-tube add a drop or two of sulphuric acid, and warm; vapour of nitric acid, HNO_3, is evolved. The fumes may be condensed by passing them through a bent delivery-tube into a second test-tube which is kept cold. The delivery-tube should not be fitted to the first test-tube by means of a cork as in the preparation of hydrochloric acid—because the nitric acid vapours would strongly act on it—but by means of plaster of Paris, a paste of which sets hard on being put aside for a short time, and is unaffected by the acid.

On a somewhat larger scale, nitric acid may be prepared by heating, in a stoppered retort, a mixture of equal weights of potassium nitrate and sulphuric acid; nitric acid distils over, and acid potassium sulphate remains:—

$$\underset{\substack{\text{Potassium}\\\text{nitrate}}}{KNO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid}}}{H_2SO_4} = \underset{\substack{\text{Nitric}\\\text{acid}}}{HNO_3} + \underset{\substack{\text{Acid potassium}\\\text{sulphate}}}{KHSO_4}$$

The acid potassium sulphate is readily converted into neutral sulphate (*Potassii Sulphas,* B.P.) by dissolving in water, adding potassium carbonate until effervescence ceases, filtering, and setting aside to crystallize.

Sodium nitrate, on account of its cheapness, is the nitrate from which manufacturers now usually prepare nitric acid.

Pure nitric acid, HNO_3, is a colourless liquid of specific gravity 1·52. The most concentrated acid met with in commerce has a specific gravity of 1·5 and contains 93 per cent. of real nitric acid; it fumes disagreeably, is unstable, and, except as an escharotic, is seldom used. The British Pharmacopœia contains three nitric acids:—Fuming nitric acid, specific gravity 1·5; *Acidum Nitricum*, prepared as above, of specific gravity 1·42 and containing 70 per cent. of real acid; and *Acidum Nitricum Dilutum*, specific gravity 1·101, containing nearly 17½ (17·44) per cent. Either of the more concentrated acids, although containing water, is usually termed "nitric acid." The official nitric acid, of specific gravity 1·42, is not a definite hydrous acid although its composition approximates to the formula $2HNO_3,3H_2O$; it distils at 250° F. (121° C.), without change. If a less concentrated acid be heated, it loses water; if a more concentrated acid be heated, it loses nitric acid, until the density of 1·42 is reached. *Aqua fortis* is an old name for nitric acid (*Aqua fortis simplex*, specific gravity 1·22 to 1·25; *Aqua fortis duplex*, 1·36). The "concentration" of a specimen of nitric acid is determined by volumetric analysis. *Nitric anhydride*, N_2O_5 (sometimes, but erroneously, called *anhydrous nitric acid*) is a solid crystalline substance formed on passing dry chlorine over dry silver nitrate.

Metals reduce nitric acid to the various oxides of nitrogen or even to nitrogen itself, according to the concentration of acid, the temperature, and the amount of nitrate present. With certain metals, such as zinc and iron, and moderately dilute nitric acid, some ammonium nitrate is formed. Thus, with zinc,—

$$10HNO_3 + 4Zn = 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

Aqua Regia.—A mixture of three fluid ounces of nitric acid (B.P.), four of hydrochloric acid (B.P.), and twenty-five of water forms the *Acidum Nitro-hydrochloricum Dilutum* of the British Pharmacopœia. The mixture should be set aside for a week in summer or a fortnight in winter, to insure complete interaction and full development of the chief active product, chlorine.

Diluted nitro-hydrochloric acid may attack organic matter with evolution of nitrous gases, hence it should not be dispensed with tinctures, etc., without further dilution.

A mixture of concentrated nitric and hydrochloric acids is known as *aqua regia* from its property of dissolving gold, the king of metals, the action being effected by the chlorine which is liberated.

$$\underset{\text{Nitric acid}}{HNO_3} + \underset{\text{Hydrochloric acid}}{3HCl} = \underset{\text{Nitrosyl chloride}}{NOCl} + \underset{\text{Water}}{2H_2O} + \underset{\text{Chlorine}}{Cl_2}$$

Nitrosyl chloride is an example of the class of compounds known as acid chlorides, or acichlorides, formed by the substitution of chlorine (Cl) for hydroxyl (OH) in an acid; thus nitrosyl chloride may be formed from nitrous acid NO·OH. The substitution of Cl for OH is often useful in deciding how the oxygen and hydrogen in a substance are combined, for it is probable that a univalent atom like Cl can only be substituted for another univalent atom or radical, and therefore if it replaces O and H they must be present as hydroxyl (– O – H).

Analytical Reactions of Nitrates.

1. To a solution of any nitrate (*e.g.* KNO_3) add sulphuric acid and then copper turnings, and warm; colourless nitric oxide, NO, is evolved, which at once unites with the oxygen in the tube, giving *red fumes* of nitrogen peroxide, NO_2.

$$2KNO_3 + 5H_2SO_4 + 3Cu = 2NO + 3CuSO_4 + 4H_2O + 2KHSO_4\text{ ; then } 2NO + O_2 = 2NO_2$$

Performed on a larger scale, in a vessel to which a delivery-tube is attached, the interaction of nitric acid and copper is the process generally adopted for the preparation of nitric oxide.

Small quantities of nitrates may be overlooked when this test is employed, the colour of the red fumes not being very intense.

Undiluted nitric acid poured upon copper turnings gives rise to the formation of dense red vapours which contain nitrogen peroxide, NO_2, nitrous anhydride, N_2O_3, nitric oxide, NO, and even nitrogen, N_2, the reaction varying somewhat according to the temperature of the mixture and (Ackworth) the quantity of cupric nitrate in solution. With ordinary copper, dilute nitric acid gives nitric oxide, $3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$.

Pure nitric oxide may be obtained by treating mercury with a mixture of sulphuric and nitric acids; or by treating a mixture of potassium nitrate 1 part, and ferrous sulphate 4 parts, with sulphuric acid and a small quantity of water.

2. To a cold solution of a nitrate, even if very dilute, add three or four crystals of ferrous sulphate, shake gently for a minute, in order that some of the sulphate may become dissolved, and then pour some concentrated sulphuric acid down the side of the test-tube, so that it may form a layer at the bottom: a dark-brown or black coloration will appear between the acid and the supernatant liquid.

This is a very delicate test for nitrates. Nitrites give the reaction without the addition of sulphuric acid. The dark colour is due to the formation of a compound by the interaction of nitric oxide with a portion of the ferrous salt. The nitric oxide is liberated from the nitrate by the reducing action of the hydrogen of the sulphuric acid, the sulphuric radical of which is absorbed by another portion of the ferrous sulphate, the latter thereby becoming converted into ferric sulphate.

$$2HNO_3 + 3H_2SO_4 + 6FeSO_4 = 4H_2O + 3Fe_2(SO_4)_3 + 2NO$$

The process of oxidation is one frequently employed in experimental chemistry; and nitrates, from their richness in oxygen, and the readiness with which they part with some of it, are the oxidizing agents often selected for the purpose. In the operation they may so decompose as to yield a metallic oxide, nitric oxide, and oxygen. Hydrogen nitrate (nitric acid) commonly yields water, and the other substances mentioned, as shown by the following equation:—$4HNO_3 = 2H_2O + 4NO + 3O_2$.

When nitrates, other than nitric acid, are used for the purpose of oxidation, a strong acid, generally sulphuric, is usually added in order that nitric acid may be formed, the latter splitting up more readily than most other nitrates.

The five oxides of nitrogen have now been mentioned, namely :—

Nitrous oxide (laughing-gas) . .	N_2O
Nitric oxide	NO
Nitrous anhydride	N_2O_3
Nitrogen peroxide*	NO_2 or N_2O_4
Nitric anhydride	N_2O_5

Nitrous oxide is a colourless gas, not altered on exposure to air. Nitric oxide is also colourless, but gives red fumes in the air, owing to combination with oxygen, NO_2 being formed. Nitrous anhydride forms a red vapour condensible to a blue liquid, recent experiments proving that the red vapour is merely a mixture of nitric oxide, NO, and nitrogen peroxide, NO_2; it is only in the liquid state (at or below $-21°$ C.) that the compound N_2O_3 exists. Nitrogen peroxide is a red vapour condensible to an orange liquid. Nitric anhydride is a colourless crystalline solid. The two anhydrides, by interaction with water, yield respectively nitrous acid, HNO_2 (stable at low temperatures but decomposed on heating), and nitric acid, HNO_3. Nitrous oxide is also probably an anhydride, corresponding to hyponitrous acid, $H_2N_2O_2$. The silver and sodium salts of the latter have the formulæ $Ag_2N_2O_2$ and $Na_2N_2O_2$.

The compounds of nitrogen and oxygen, formulated above, furnish a good illustration of the law of multiple proportions.

3. Direct the blowpipe-flame against a piece of charcoal until a spot is red-hot; now place on the spot a fragment of a nitrate; deflagration ensues.

This reaction does not distinguish nitrates from chlorates, but indicates the presence of these or other highly oxidized salts, even when the quantities are small and other substances are mixed with them.

Gunpowder is an intimate mechanical mixture of 75 parts of nitre, 15 to 12½ parts of charcoal, and 10 to 12½ parts of sulphur. In order to avoid explosions, the ingredients must be separately ground, then moistened with water and mixed to a paste, which is afterwards granulated and carefully dried. When fired it may be said to yield potassium sulphide, K_2S (the white smoke), nitrogen, N_2, carbonic oxide, CO, and carbonic anhydride, CO_2, though the decomposition is seldom complete. The sudden production of a large quantity of highly heated gas from a small quantity of a cold solid is sufficient to account for the effects produced by gunpowder when fired.

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* At low temperatures nitrogen peroxide is represented by the formula N_2O_4. The molecules of N_2O_4 decompose, however, on gently warming to form $2NO_2$.

4. To nitric acid or any other nitrate add a solution of sulphindigotic acid (indigo sulphate); the blue colour is discharged. Free chlorine also destroys the colour of this reagent.

Solution of Indigo Sulphate, B.P.—Sulphindylic or Sulphindigotic Acid is indigotin-disulphonic acid, $C_{16}H_8(HSO_3)_2N_2O_2$, and is made by digesting 0·2 gramme of dry finely powdered indigo in 2 cubic centimetres of concentrated sulphuric acid in a test-tube for an hour, the mixture being kept hot by means of a water-bath; the blue liquid is then poured into 198 cubic centimetres of sulphuric acid, the whole well shaken, set aside, and the clear liquid decanted.

Antidote.—In cases of poisoning by nitric acid, solution of sodium carbonate (common washing soda) or magnesia and water may be administered as antidote.

QUESTIONS AND EXERCISES

Trace the origin of nitrates.—In what does cubic nitre differ from prismatic nitre?—Describe a process by which potassium nitrate may be obtained artificially.—State the difference between ordinary nitre and sal prunella.—What is the acid radical of the nitrates?—How is the official nitric acid prepared?—Give the properties of nitric acid.—What reactions occur when concentrated nitric and hydrochloric acids are mixed?—How is nitric oxide prepared?—Enumerate and explain the tests for nitrates.—What reduction products may be obtained from nitric acid when it is employed as an oxidizing agent?—How is nitrous oxide prepared?—Enumerate the five oxides of nitrogen.—What is the nature of gunpowder?—What quantity of cubic nitre will be required to produce ten carboys of official nitric acid, each containing 114 lbs.? *Ans.*, 1077 lbs.

HYPOCHLOROUS ACID, HClO, and other Hypochlorites

Experiment.—Place a few grains of red mercuric oxide (or better, a small quantity of moist freshly-precipitated yellow mercuric oxide) in a test-tube, half fill the tube with chlorine water, well shake the mixture, and filter; the resulting liquid is a solution of hypochlorous acid, mercuric oxychloride remaining undissolved:—

$$2HgO + 2Cl_2 + H_2O = 2HClO + Hg_2OCl_2$$

By the interaction of hypochlorous acid and oxides or hydroxides, other pure hypochlorites are formed:—$HClO + NaOH = NaClO + H_2O$.

The action of chlorine on metallic hydroxides gives rise to "bleaching salts," which are either mixtures of hypochlorite and chloride, or compounds intermediate between hypochlorite and chloride (*see* p. 125, *Calx Chlorinata*, B.P., also p. 91, *Liquor Sodæ Chlorinatæ*, B.P.)

$$\begin{aligned} Cl_2 + 2NaOH &= (NaClO,\ NaCl) + H_2O\,; \\ 2Cl_2 + 2Ca(OH)_2 &= (CaCl_2O_2,\ CaCl_2) + 2H_2O. \end{aligned}$$

The action of strong acids on "bleaching salts" results in the evolution of chlorine; hence the great value of chlorinated lime in bleaching operations:—

$$(CaCl_2O_2,\ CaCl_2) + 2H_2SO_4 = 2Cl_2 + 2CaSO_4 + 2H_2O$$

On exposure to air solutions of hypochlorites are slowly decomposed with liberation of hypochlorous acid, recognisable by its peculiar odour:—

$$2NaClO + CO_2 + H_2O = 2HClO + Na_2CO_3$$

The peculiar odour of this acid, the liberation of chlorine on the addition of a strong acid, and their bleaching powers, are the characters on which to rely in searching for hypochlorites.

CHLORIC ACID, $HClO_3$, and other Chlorates

Chlorates are formed by boiling aqueous solutions of the bleaching salts (chlorinated lime, chlorinated soda, chlorinated potash). Heat thus converts—

$3(NaClO, NaCl)$ Chlorinated soda	into	$NaClO_3$ Sodium chlorate	and	$5NaCl$ Sodium chloride
$3(KClO, KCl)$ Chlorinated potash	into	$KClO_3$ Potassium chlorate	and	$5KCl$ Potassium chloride
$3[Ca(ClO)_2, CaCl_2]$ Chlorinated lime	into	$Ca(ClO_3)_2$ Calcium chlorate	and	$5CaCl_2$ Calcium chloride

Potassium Chlorate

Potassium Chlorate (*Potassii Chloras*, B.P.), is commercially made by saturating with chlorine gas a moistened mixture of 3 parts of potassium chloride and 10 of calcium hydroxide, and well boiling the product. Chlorinated lime is first formed; this, on continued boiling with water, splits up into calcium chloride and calcium chlorate; and the latter interacting with the potassium chloride yields calcium chloride and potassium chlorate.

$$6Ca(OH)_2 + 6Cl_2 = 3[CaCl_2, Ca(ClO)_2] + 6H_2O;$$
$$3[CaCl_2, Ca(ClO)_2] = Ca(ClO_3)_2 + 5CaCl_2;$$
$$Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2KClO_3$$

The operation may be conducted on a small scale by rubbing the ingredients together in a mortar in the foregoing proportions, adding enough water to make the whole assume the character of damp lumps, placing the porous mass in a funnel (loosely plugged with fragments of glass) and passing chlorine up through the mass by attaching to the neck of the funnel the tube delivering the gas. When the whole mass has become of a slight pink tint (due to a trace of permanganate from manganese present as impurity in the calcium hydroxide) it should be turned into a dish, *well* boiled with water, filtered, the filtrate evaporated if necessary, and set aside; the potassium chlorate separates in tabular monoclinic crystals, calcium chloride remaining in the mother-liquor. In this process potassium carbonate may be used in place of potassium chloride.

$$\underset{\text{Chlorine}}{6Cl_2} + \underset{\text{Potassium carbonate}}{K_2CO_3} + \underset{\text{Calcium hydroxide}}{6Ca(OH)_2} =$$

$$\underset{\substack{\text{Potassium}\\ \text{chlorate}}}{2KClO_3} + \underset{\substack{\text{Calcium}\\ \text{carbonate}}}{CaCO_3} + \underset{\substack{\text{Calcium}\\ \text{chloride}}}{5CaCl_2} + \underset{\text{Water}}{6H_2O}$$

Potassium chlorate is now prepared on the commercial scale by the electrolysis of a solution of potassium chloride.

Potassium chlorate is soluble in water to the extent of 6 or 7 parts in 100 at ordinary temperatures. It is usually administered medicinally in aqueous solution, sometimes also in lozenges (*Trochiscus Potassii Chloratis,* B.P.). Potassium chlorate must on no account be rubbed with sulphur or sulphides, in a mortar or otherwise, friction of such mixtures often giving rise to violent explosions.

Potassium chlorate when heated to a temperature not greatly beyond its fusing point, yields potassium chloride and oxygen, and is the salt commonly employed in the preparation of this gas for experimental purposes. If the action be carried on at as low a temperature as possible, and be arrested when one hundred parts of the chlorate have yielded 7·84 parts of oxygen, the residue will be found to contain only potassium perchlorate, $KClO_4$, and chloride; $10KClO_3 = 6KClO_4 + 4KCl + 3O_2$ (Teed). A higher temperature causes the decomposition of the perchlorate; $KClO_4 = KCl + 2O_2$. When the chlorate is heated with manganese peroxide, no perchlorate is formed.

Sodium Chlorate (*Sodii Chloras,* U.S.P), $NaClO_3$, is prepared in the same way as potassium chlorate.

Chloric acid, $HClO_3$, may be isolated by decomposing barium chlorate with dilute sulphuric acid, but is unstable, quickly decomposing into chlorine, oxygen, and perchloric acid.

Analytical Reactions of Chlorates.

1. To a solution of a chlorate add solution of silver nitrate; no precipitate is produced, showing that silver chlorate is soluble in water. Evaporate another portion of the solution to dryness, and place the residue in a small dry test-tube (or simply drop a fragment of a chlorate into a test-tube) and heat strongly; oxygen is evolved, and may be recognised by

its power of rekindling an incandescent match inserted in the tube. Boil the residue with water, and again add solution of silver nitrate ; a white precipitate is produced which possesses all the characters of silver chloride, as described under hydrochloric acid.

2. To a small fragment of a chlorate add two or three drops of concentrated sulphuric acid ; an explosive gas, chlorine peroxide, ClO_2, is evolved, which somewhat resembles chlorine in odour, but possesses a deeper colour.

$$3KClO_3 + 2H_2SO_4 = 2ClO_2 + KClO_4 + 2KHSO_4 + H_2O.$$

Warm the upper part of the test-tube to 150° or 200° F. (65·5° to 93·3° C.), or introduce a hot wire ; a sharp explosion ensues, due to decomposition of the chlorine peroxide into chlorine and oxygen.

3. Heat a small fragment of a chlorate with hydrochloric acid ; a yellowish green gaseous mixture called *euchlorine* is evolved. Its colour is deeper than that of chlorine, hence the name (from εὖ, *eu*, well, and χλωρὸς, *chlōros*, green). It is really a mixture of that element with chlorine peroxide.

4. Direct the blowpipe-flame against a piece of charcoal until a spot is red-hot, and then place on the spot a fragment of a chlorate ; deflagration ensues, as in the case of nitrates.

Perchloric acid, $HClO_4$. — Crude potassium perchlorate obtained as already described, is boiled (in a fume-cupboard) with hydrochloric acid to decompose any chlorate that may be present, and then separated from chloride by washing and crystallization, chloride being far more soluble in water than perchlorate. Perchloric acid is then obtained by distilling the potassium perchlorate with sulphuric acid ; it is stable, and is occasionally administered in medicine.

Table of the Chlorine Acids.

Hydrochloric acid	HCl
Hypochlorous acid	$HClO$
Chloric acid	$HClO_3$
Perchloric acid	$HClO_4$

The acid radicals of the above chlorine acids are univalent, as indicated in the various formulæ.

Bromates

Bromates are salts closely resembling chlorates and iodates. The formula of bromic acid is $HBrO_3$. The presence of bromates, as impurity, in bromides is shown by the production of a yellow colour, due to the liberation of bromine, on the addition of dilute sulphuric acid.

$$5KBr + KBrO_3 + 6H_2SO_4 = 6KHSO_4 + 3H_2O + 3Br_2$$

Iodates

Iodic Acid, HIO_3.—Iodine is warmed in a flask with five times its weight of fuming nitric acid (sp. gr. 1·5), in a fume-cupboard, until all action ceases. On cooling, iodic acid separates in small pyramidal crystals. These are separated, the residual liquid evaporated to dryness to remove excess of nitric acid, the residue and the first crop of crystals dissolved in a small quantity of boiling water, and the solution set aside to crystallize. Neutralized with carbonates or hydroxides, it yields *iodates.*

Potassium iodate and sulphurous acid mutually interact with elimination of iodine (and formation of a blue colour, if starch be present). Sulphurous acid occurring as an impurity in acetic and other acids may thus be detected.

$$2KIO_3 + 5H_2SO_3 = I_2 + 3H_2SO_4 + 2KHSO_4 + H_2O$$

Ferric Iodate, or rather *Oxyiodate,* $Fe_2O(IO_3)_4$, $8H_2O$, is precipitated on adding a solution of ferric chloride to solution of potassium iodate. When heated with sulphuric acid and potassium bichromate, most iodides are decomposed, yielding iodine and a sulphate of the metal; silver iodide, however, is an exception, as, though it gradually dissolves, no iodine is separated, and on diluting the solution and allowing it to cool, a yellow precipitate consisting of impure silver iodate is deposited.

QUESTIONS AND EXERCISES

How may hypochlorous acid be formed?—By what reaction is chlorine eliminated from hypochlorites? State the general reaction by which chlorates are formed.—Give details of the preparation of potassium chlorate.—Mention the properties of potassium chlorate.—What decompositions occur when potassium chlorate is heated?—Find the formula weight of potassium chlorate.—What weight of oxygen is produced when 1 oz. of potassium chlorate is completely decomposed, and how much potassium chloride remains?—One hundred cubic inches of oxygen, at 60° F. and barometer at 30 inches, weighing 34·203 grains, and one gallon containing 277¼ cubic inches, what weight of potassium chlorate will be required to yield 10 gallons of the gas? *Ans.*, 5½ oz.—Calculate the weight of potassium chloride obtainable from 100 parts of potassium chlorate.—How may the presence of chlorides in chlorates be demonstrated?—Mention the tests for chlorates. — Give the formula of chlorine peroxide. — What is euchlorine?—How is perchloric acid prepared? — Enumerate the chlorine acids.—How may iodic acid be made?

ACETIC ACID, $HC_2H_3O_2$, and other Acetates

Source.—Acetic acid is said to occur naturally in small quantity in certain plant-juices and animal fluids, but is usually an artificial product. Much acetic acid is produced during the destructive distillation of wood. When first discovered in this operation the acid was regarded as a new one, and was named *pyroligneous acid*, a hybrid word from πῦρ, *pūr*, fire, and *lignum*, wood, a term still retained for the crude acid. The latter, neutralized by calcium carbonate, the solution evaporated to dryness, and the residue gently heated to drive off volatile tarry matters, yields calcium acetate. Acetic acid is obtained in a state of purity (mixed with water only) by starting from this crude calcium acetate, converting it into sodium acetate, recrystallizing the latter and distilling it with dilute sulphuric acid. Diluted acetic acid is sometimes sold as *white vinegar*, one of the many varieties of *vinegar*. It has been known as *wood vinegar* for the past sixty or seventy years. It is generally coloured brown with caramel to meet the taste of the public. In Germany and France large quantities of acetic acid are made by the oxidation of the alcohol in inferior wines, in the presence of a bacterium called *Mycoderma Aceti* (the *Bacterium Mycodermi* of Cohn); hence the *white-wine* and *red-wine vinegars* (*vinegar*, from the French *vin*, wine, and *aigre*, sour). This bacterium may be cultivated, and the manufacture of vinegar from alcohol and water is carried out, by its aid, on the large scale. In England also the domestic form of acetic acid (brown vinegar) commonly has an alcoholic origin: infusion of malt and unmalted grain, or sometimes the latter alone after treatment with sulphuric acid, is fermented; and the resulting alteration of its sugar, instead of being arrested when the product is an alcoholic liquid, a sort of beer, is allowed to go on to the next stage, acetic acid; it usually contains from 3 to 6 per cent. of actual acetic acid or hydrogen acetate, $HC_2H_3O_2$. Different strengths of vinegar are sold under the numbers 16, 18, 20, 22, and 24, corresponding to the number of grains of anhydrous sodium carbonate neutralized by one imperial fluid ounce of the vinegar, or, broadly, to 4, $4\frac{1}{2}$, 5, $5\frac{1}{2}$ and 6 per cent. of acetic acid respectively. All of these "brewed vinegars" are further coloured with caramel, to suit the popular taste. *Vinegar* is a generic term applicable to any one or to all varieties. Its essential component is acetic acid.

Official Vinegars.—The so-called Vinegar of Cantharides (*Acetum Cantharidis*, B.P.) is a solution of the active principle of cantharides in moderately concentrated acetic acid. The Vinegars of Squill (*Acetum Scillæ*, B.P.), of Ipecacuanha (*Acetum Ipecacuanhæ*, B.P.), and of Urginea (*Acetum Urgineæ*, B.P. Add. 1900), as well as *Acetum Opii*, U.S.P., or "black drop," contain dilute acetic acid, that is, *wood vinegar*. *Vinegar of Mylabris* (*Acetum Mylabridis*, B.P. Add. 1900) contains equal volumes of glacial acetic acid and distilled water.

The acetic radical, $C_2H_3O_2'$, is univalent.

Acetic acid is regarded as containing the radical *acetyl* (C_2H_3O) united with *hydroxyl* (OH), and the acetates as containing metal in place of the hydrogen of the hydroxyl group. By interaction with phosphorus trichloride, acetic acid yields acetyl chloride, C_2H_3OCl. Acetyl chloride and sodium acetate interact to give sodium chloride and acetic anhydride.

$$\begin{array}{ll} C_2H_3O & Cl \\ C_2H_3OO & Na \end{array} = (C_2H_3O)_2O + NaCl$$

By interaction with water, acetic anhydride yields acetic acid: $(C_2H_3O)_2O + H_2O = 2C_2H_4O_2$.

Note on Anhydrides.—Up to this point an anhydride has been regarded as a substance derived from an acid by removal of the *whole* of the hydrogen of the acid, together with as much of its oxygen as with the hydrogen forms water. This does not apply to acetic anhydride, and must therefore be somewhat qualified. An *anhydride* is derived from an acid, the acid having lost the whole of its *replaceable* hydrogen, and as much oxygen as is necessary to form water with that hydrogen.

The relation of acetic acid to alcohol will be evident from the following equation representing the formation of the acid:—

$$\underset{\text{Alcohol}}{C_2H_6O} + O_2 = \underset{\text{Acetic acid}}{C_2H_4O_2} + H_2O$$

Acetates in aqueous solution are liable to decomposition. In solution of morphine acetate a fungoid growth occasionally forms, acetic acid disappears, and morphine is deposited. Solution of ammonium acetate is liable to a similar change, gradually becoming alkaline.

Experiment.—To a few grains of sodium acetate in a test-tube, add dilute sulphuric acid, and heat; acetic acid is evolved, and may be condensed by passing it through a bent tube adapted to the test-tube by means of a cork in the usual way.

$$\underset{\substack{\text{Sodium}\\\text{acetate}}}{NaC_2H_3O_2} + \underset{\substack{\text{Sulphuric}\\\text{acid}}}{H_2SO_4} = \underset{\text{Acetic acid}}{HC_2H_3O_2} + \underset{\substack{\text{Acid sodium}\\\text{sulphate}}}{NaHSO_4}$$

The above is the process by which acetic acid is obtained from sodium or calcium acetate on the large scale. As in the cases of nitric and hydrochloric acids, the term "acetic acid" is usually applied to the aqueous solution of the acid. *Acidum Aceticum*, B.P., contains 33 per cent. of hydrogen acetate, $HC_2H_3O_2$. *Acidum Aceticum Dilutum*, B.P., contains about $4\frac{1}{4}$ (4·27) per cent. Glacial acetic acid, $HC_2H_3O_2$, contains no water. It solidifies to a crystalline mass at temperatures below 63° F. (17·2° C.), hence the appellation *glacial* (from *glacies*, ice). Good commercial glacial acetic acid (*Acidum Aceticum Glaciale*, B.P.) does not contain more than 1 per cent. of water; it solidifies when cooled, and again liquefies at about 60° F. (15·5° C.); its specific gravity is 1·058. Although water is specifically lighter than this acetic acid, yet the addition of water at first raises the sp. gr. of the acid; evidently, therefore, contraction takes place on mixing the liquids: after 10 per cent. has been added, the addition of more water produces the usual effect of dilution of a liquid with one specifically lighter—namely, lowering of the specific gravity. Glacial acetic acid mixes readily with most oils.

Analytical Reactions of Acetates.

1. To an acetate add sulphuric acid, and heat the mixture; the characteristic odour of acetic acid is evolved.

Note.—Iodine, sulphurous anhydride, and other substances which possess a powerful odour, may mask that of acetic acid.

2. Repeat the above reaction, a few drops of alcohol being first added to the acetate; acetic ether (ethyl acetate, $C_2H_5C_2H_3O_2$), possessing a characteristic pleasant odour, is evolved.

3. Heat a fragment of a dry acetate (potassium, sodium calcium or barium acetate, for example) in a test-tube, and notice the odour of the gaseous products of the decomposition; amongst them is *acetone*, C_3H_6O, the odour of which is characteristic. Blackening takes place in most cases. A carbonate remains in the test-tube. (*See* tests for carbonates.)

4. To a solution of an acetate, made neutral by the addition of acid or alkali, as the case may be, add a few drops of neutral solution of ferric chloride; a deep-red liquid results, owing to the formation of ferric acetate, $Fe(C_2H_3O_2)_3$. Boil; a red precipitate of ferric oxyacetate is formed, leaving the liquid colourless.

Analytical Note.—The student should observe that all normal acetates are soluble in water. Silver acetate, $AgC_2H_3O_2$, and mercurous acetate, $HgC_2H_3O_2$, are only sparingly soluble in cold water, but the fact can seldom be utilized in analysis. Hence, precipitation not being available, peculiarities of colour and odour, the next best characters on which to rely, are usually adopted as means by which acetates may be detected. Most acetates, like many other organic compounds, char when heated to a high temperature.

QUESTIONS AND EXERCISES

What is the formula of acetic acid?—State the relation of acetic acid to other acetates.—What is the molecular weight of acetic acid?—Name the sources of acetic acid.—What is pyroligneous acid?—From what compound is the acetic acid of most foreign and English varieties of vinegar derived?—What is the nature of the "Vinegars" of Pharmacy?—How may acetic acid be obtained from sodium acetate?—How much hydrogen acetate is contained in each of the official acetic acids?—Enumerate the tests for acetates.

HYDROSULPHURIC ACID, H_2S, and other Sulphides

Occurrence and varieties of Sulphur.—The acid radical of *hydrogen sulphide, hydrosulphuric acid, sulphydric acid,* or *sulphuretted hydrogen* and other sulphides, is sulphur, S. Sulphur occurs free in nature, and also in combination with metals, as already stated in describing the ores of some of the metals. It also occurs in coal, chiefly as iron pyrites, and sulphur compounds are obtained, as waste-products, in the manufacture of coal-gas. Most of the sulphur used in medicine is imported from Sicily, where it occurs chiefly associated with blue clay. It is purified by fusion, sublimation, or distillation. Melted and poured into moulds, it forms *roll sulphur.* It is slightly volatile, even on a water-bath. If distilled, and the vapour carried into large chambers, so that it may be condensed rapidly, it forms crystals which are so minute as to give the sulphur a pulverulent character; this is *sublimed sulphur* (*Sulphur Sublimatum,* B.P.), or *flowers of sulphur:* "solution of ammonia, agitated with it, and filtered, does not on evaporation leave any residue (absence of arsenium sulphide)." Sulphur, washed with dilute ammonia to remove traces of sulphuric acid (often 0·1 per cent., resulting from very slow oxidation of sulphur in ordinary moist air), or, possibly, arsenious sulphide constitutes *Sulphur Lotum,* U.S.P. The third common form, *milk of sulphur* (*Sulphur Præcipitatum,* B.P.), will be noticed subsequently. Sulphur also occurs in nature in combination as a constituent of animal and vegetable tissues, as sulphurous anhydride, SO_2, in volcanic vapours, and as hydrogen sulphide in some mineral waters. Sulphur exists in several allotropic forms, of which the following four may be noticed:—1. Octahedral sulphur—the native and most stable form. 2. Prismatic sulphur, obtained by melting the ocathedral variety, and cooling until a crust forms. 3. Plastic sulphur, obtained by heating melted sulphur to a temperature of 440° C. (836° F.), and pouring into cold water. 4. Amorphous sulphur, obtained in the proportion of 5-6 per cent. when the octahedral variety is sublimed.

Allotropy.—The existence of more than one variety of the same elementary substance (as instanced in the varieties of sulphur enumerated above) illustrates what is known in chemistry as allotropy (ἄλλος, *allos*, another; τρόπος, *tropos*, condition). Other instances are met with in the different forms of carbon, phosphorus, etc.

Black sulphur or *Sulphur vivum nigrum* is the misleading name of a greyish mineral mixture of sulphur with a great variety of impurities, generally including arsenic. The article should not be used for any medicinal purpose.

Quantivalence.—Sulphur behaves as a sexivalent element in sulphuric anhydride, SO_3, a substance which will be noticed under sulphuric acid, and as quadrivalent in sulphurous anhydride, SO_2, while it is frequently bivalent, as in hydrogen sulphide, H_2S.

Molecular Formula.—At temperatures between the boiling point of sulphur (448·4° C.) and about 1000° C., the vapour density of sulphur gradually diminishes as the temperature rises. Above 1000° C., or so, it is constant and then corresponds to the molecular formula S_2.

Precipitated Sulphur

Experiment 1.—Prepare *Precipitated Sulphur* (*Sulphur Præcipitatum*, B.P.), or *Milk of Sulphur*, by boiling a few grains of flowers of sulphur (5 parts) with calcium hydroxide (3 parts) and water (20 parts) in a test-tube (larger quantities in an evaporating-basin), filtering, and (reserving a small portion of the filtrate) adding dilute hydrochloric acid until the well-stirred milky liquid still has a faintly alkaline reaction to test-paper; sulphur is precipitated, and may be collected on a filter, washed, and dried (at about 130° F., 54·4° C.). Excess of acid must be avoided in order to prevent contamination of the precipitate with traces of arsenious sulphide (from the decomposition of any thiarsenite, produced from arsenious sulphide present as impurity in the sulphur employed).

This is the method of the Pharmacopœia.—Calcium polysulphide and thiosulphate are first formed:—

$$\underset{\substack{\text{Calcium}\\\text{hydroxide}}}{3Ca(OH)_2} + \underset{\text{Sulphur}}{6S_2} = \underset{\substack{\text{Calcium}\\\text{polysulphide}}}{2CaS_5} + \underset{\substack{\text{Calcium}\\\text{thiosulphate}}}{CaS_2O_3} + \underset{\text{Water}}{3H_2O}$$

On adding the acid, both salts are decomposed and (partly in consequence of an intermediate reaction) sulphur separates:—

$$\underset{\substack{\text{Calcium}\\\text{polysulphide}}}{2CaS_5} + \underset{\substack{\text{Calcium}\\\text{thiosulphate}}}{CaS_2O_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid}}}{6HCl} = \underset{\substack{\text{Calcium}\\\text{chloride}}}{3CaCl_2} + \underset{\text{Water}}{3H_2O} + \underset{\text{Sulphur}}{6S_2}$$

The calcium polysulphide yields hydrogen sulphide and milk-white sulphur on the addition of the acid. The calcium thiosulphate then yields sulphurous anhydride as well as yellowish sulphur. The gases interact and give sulphur and water, very little hydrogen sulphide escaping: this is the intermediate reaction just alluded to. A little pentathionic acid (p. 337) is also said to be formed.

$$4H_2S + 2SO_2 = 3S_2 + 4H_2O$$

Sulphur Lozenge (*Trochiscus Sulphuris,* B.P.) contains 5 grains of precipitated sulphur, 8 grains of sugar, and 1 grain each of gum acacia and cream of tartar, made into a mass with 1 minim each of mucilage and tincture of orange, and dried.

Experiment 2.—Calcareous Precipitated Sulphur. The *old* "Milk of Sulphur."—To a sulphur solution prepared as before (or to the reserved portion) add a little dilute sulphuric acid; the precipitate is in this case largely mixed with calcium sulphate:—

$$\underset{\substack{\text{Calcium}\\\text{polysulphide}}}{2CaS_5} + \underset{\substack{\text{Calcium}\\\text{thiosulphate}}}{CaS_2O_3} + \underset{\substack{\text{Sulphuric}\\\text{acid}}}{3H_2SO_4} + \underset{\text{Water}}{3H_2O} = \underset{\text{Calcium sulphate}}{3(CaSO_4,\ 2H_2O)} + \underset{\text{Sulphur}}{6S_2}$$

Place a little of each of these specimens of "precipitated sulphur," with a drop of the supernatant liquid, on a strip of glass, place a cover-glass upon each, and examine the precipitates under a microscope; the pure sulphur will be found to consist of minute grains or globules, the calcareous precipitate to contain comparatively large crystals (hydrous calcium sulphate).

Note.—Some of the precipitated sulphur met with in trade in England, is still thus mixed with calcium sulphate, most of such specimens containing two-thirds of their weight of the latter substance. Formerly, purchasers were so accustomed to the satiny appearance of the mixed article as to regard real sulphur with suspicion, sometimes refusing to purchase it. The mixed article is, certainly, somewhat more easily miscible with aqueous liquids.

The calcareous precipitated sulphur yields a white ash (anhydrous calcium sulphate) when a little is burnt off on the end of a table-knife or spatula or in a porcelain crucible. To ascertain, exactly, the amount of the sulphate, place a weighed quantity in a tared porcelain crucible, and heat till no more vapours are evolved. The weight of the residual anhydrous calcium sulphate ($CaSO_4 = 135{\cdot}05$), multiplied by 1·265, is the amount of hydrous calcium sulphate ($CaSO_4, 2H_2O = 170{\cdot}8$) present in the original quantity of calcareous sulphur.

Hydrogen Sulphide, Hydrosulphuric Acid, or Sulphuretted Hydrogen. — The preparation of hydrogen sulphide was described on p. 102.

Hydrosulphides.—Besides ammonium hydrosulphide, which has already been referred to on p. 102, solutions of sulphides and of other hydrosulphides may be obtained by the interaction of hydrogen sulphide with solutions of hydroxides. Sodium and potassium sulphides and hydrosulphides, Na_2S and K_2S, and NaSH and KSH, are the most important of these substances:

$$2KOH + H_2S = K_2S + 2H_2O\,;$$
$$NaOH + H_2S = NaSH + H_2O.$$

Like ammonium hydrosulphide, they act as solvents for the arsenium, antimony, and stannic sulphides, forming with them thio-salts. They all dissolve sulphur, producing yellow solutions.

Analytical Reactions of Sulphides and Hydrosulphides.

To a sulphide or hydrosulphide add a few drops of hydrochloric acid; hydrogen sulphide will probably be evolved, recognisable by its odour. If the sulphide is not acted upon by the acid, or if free sulphur be under examination, mix a minute portion with a fragment of solid caustic potash or soda, and fuse in a silver capsule (or old spoon). When cold, place a drop of dilute hydrochloric acid on the fused mass; hydrogen sulphide is evolved, and a black stain, due to silver sulphide, Ag_2S, is left on the silver.

The most convenient reagent for detecting a sulphide in solution of ammonia is copper ammonio-sulphate, which gives a black precipitate of cupric sulphide if a sulphide be present.

Sulphur Iodide, S_2I_2 (*Sulphuris Iodidum*, B.P.), has already been mentioned under Iodine. A *chloride*, S_2Cl_2, and *bromide*, S_2Br_2, may also be formed from the elements. A mixture of sulphur and sulphur chloride is sometimes met with under the name of *sulphur hypochloride.*

QUESTIONS AND EXERCISES

In what forms does sulphur occur in nature?—State the modes of preparation of the three chief commercial varieties of sulphur.—In what respect does the atom of sulphur vary in quantivalence?—Describe the preparation of hydrogen sulphide. What are the characters of pure precipitated sulphur?—Give equations explanatory of the reactions which occur in preparing precipitated sulphur.—Describe the microscopic test for calcareous precipitated sulphur.—Mention a method of detecting calcium sulphate in precipitated sulphur.—Mention the tests for sulphides, and the character by which hydrogen sulphide is distinguished from other sulphides.—How are sulphides insoluble in acids tested for sulphur?—How would you detect a trace of sulphide in ammonia solutions?

SULPHUROUS ACID [H_2SO_3], and other Sulphites

When sulphur is burnt in the air, it combines with oxygen and forms sulphurous anhydride, SO_2, occasionally, but erroneously, called sulphurous acid. It is a pungent, colourless gas, readily liquefied on being passed through a tube cooled by a *freezing-mixture* composed of two parts of well-powdered ice (or of snow) with one part of common salt. If sulphurous anhydride is passed into water, heat is evolved and some sulphurous acid [H_2SO_3], is apparently formed in solution.

Hydrous sulphurous acid may be obtained in crystals by freezing a concentrated aqueous solution, but it is very unstable.

Quantivalence.—The acid radical of the sulphites is bivalent (SO_3''). Acid sulphites, such as acid potassium sulphite, $KHSO_3$, and normal sulphites, such as sodium sulphite, Na_2SO_3, are known.

Note.—The sulphites are so named in accordance with the usual rule that salts corresponding with acids whose names end in *ous* have a name ending in *ite.*

Experiment.—To a few drops of sulphuric acid in a test-tube add a piece of charcoal and apply heat; sulphurous anhydride (mixed with carbonic anhydride) is evolved, and may be conveyed through a bent tube into a small quantity of cold water in another test-tube. Larger quantities of the gas may be made in a flask. The product is *Acidum Sulphurosum,* B.P. It contains, if fairly saturated, about 5 per cent. of sulphurous anhydride, corresponding to about $6\frac{1}{2}$ (6·4) per cent. of sulphurous acid.

$$\underset{\substack{\text{Sulphuric}\\\text{acid}}}{2H_2SO_4} + \underset{\text{Carbon}}{C} = \underset{\substack{\text{Carbonic}\\\text{anhydride}}}{CO_2} + \underset{\text{Water}}{2H_2O} + \underset{\substack{\text{Sulphurous}\\\text{anhydride}}}{2SO_2}$$

Sulphurous anhydride may also be made by heating copper, mercury, or iron with concentrated sulphuric acid, a metallic sulphate being formed. Also by heating sulphur with sulphuric acid.

Sulphites are generally made by passing sulphurous anhydride into solutions of hydroxides or carbonates, or into water containing such substances in suspension. In the case of carbonates, carbonic anhydride escapes. The formula of Sodium Sulphite (*Sodii Sulphis,* B.P.) is $Na_2SO_3,7H_2O$; it occurs in colourless efflorescent prisms, soluble in water or alcohol. As "*antichlor*" it was formerly used for removing traces of chlorine from paper pulp (sodium thiosulphate is now employed). The formula of Sodium Bisulphite (*Sodii Bisulphis,* U.S.P.) is $NaHSO_3$. The so-called *Bisulphite of Lime,* used by brewers for retarding or arresting fermentation and oxidation, and employed for various antiseptic purposes, is made by passing sulphurous anhydride, SO_2, into thin milk of lime. Its specific gravity varies from 1·050 to 1·070, and it corresponds to from 4 to 6 per cent. of sulphurous anhydride. The so-called *meta-bisulphites* of potassium and sodium, used in photography, are really anhydrosulphites, $K_2S_2O_5$ and $Na_2S_2O_5$. They may be obtained by passing sulphurous anhydride into hot saturated solutions of potassium and sodium carbonates, respectively. Sulphurous anhydride is very soluble in alcohol.

Analytical Reactions of Sulphites.

1. To a sulphite (sodium sulphite, for instance,—made by passing sulphurous anhydride into solution of sodium carbonate) add a drop or two of dilute hydrochloric acid; a peculiarly pungent odour is produced (sulphurous acid).

This odour is the same as that evolved on burning sulphur. It is due, probably not to sulphurous anhydride, SO_2, but to sulphurous acid, H_2SO_3, formed by the union of the sulphurous anhydride with either the moisture of the air or that on the surface of the mucous membrane of the nose. The gas is highly suffocating.

2. To a sulphite add a little water, a fragment or two of zinc, and then hydrochloric acid; hydrogen sulphide is evolved, recognisable by its odour and by its action on a piece of paper placed like a cap on the mouth of the test-tube and moistened with a drop of solution of lead acetate (a black stain of lead sulphide being formed). The presence of sulphurous acid in acetic acid or in hydrochloric acid may be detected by means of this test:—$H_2SO_3 + 6H = H_2S + 3H_2O$.

Other Reactions.

To separate portions of a solution of a normal sulphite add barium nitrate or chloride, calcium chloride, and silver nitrate; in each case a white precipitate of a metallic sulphite results. The barium sulphite is soluble in dilute hydrochloric acid; but if a drop or two of chlorine water is first added, barium sulphate is formed, which is insoluble. The other precipitates are also soluble in dilute acids. Silver sulphite is decomposed on boiling, sulphuric acid being formed, and metallic silver set free, the precipitate darkening in colour.

To recognise the three radicals in an aqueous solution of sulphides, sulphites, and sulphates, add barium chloride, filter, and wash the precipitate. In the filtrate, sulphides are detected by the evolution of hydrogen sulphide on the addition of an acid. In the precipitate, sulphites are detected by observing the odour of sulphurous acid produced on adding hydrochloric acid, and sulphates are detected by the insolubility of barium sulphate in the acid.

QUESTIONS AND EXERCISES

What are the differences between sulphurous acid and sulphurous anhydride, sulphites and acid sulphites?—State the characters of sulphurous anhydride.—How is the official sulphurous acid prepared?—By what tests may sulphurous acid be recognised in acetic acid?—Give a method by which sulphites may be detected in presence of sulphides and sulphates.

SULPHURIC ACID, H_2SO_4, and other Sulphates

Many sulphates occur in nature. The most important of these are *heavy spar*, barium sulphate, $BaSO_4$; *gypsum*, calcium sulphate, $CaSO_4, 2H_2O$; and *Epsom salt*, magnesium sulphate, $MgSO_4, 7H_2O$.

Preparation of Sulphuric Acid.—Sulphur itself, or more usually the sulphur in iron pyrites, is first converted into sulphurous anhydride by burning in air, and this gas, by oxidation in presence of moisture, is then converted into sulphuric acid: $SO_2 + H_2O + O = H_2SO_4$. The oxygen necessary to oxidize the sulphurous anhydride may be obtained directly from the atmosphere, but the process is a very slow one.

The transference of oxygen to the sulphurous anhydride, in presence of moisture, to form sulphuric acid, is greatly hastened in practice by the use of nitric oxide. This gas, when mixed with air, takes up oxygen to form nitrogen peroxide, NO_2, which, in turn, is easily reduced again to nitric oxide by parting with half its oxygen to the moist sulphurous anhydride. The nitric oxide so liberated reunites with oxygen, again forming nitrogen peroxide which again undergoes similar reduction to nitric oxide, so that the process becomes virtually a continuous one, a small proportion of nitric oxide sufficing to convert relatively large quantities of sulphurous anhydride, oxygen, and water into sulphuric acid.

The nitric oxide is in the first instance obtained from nitric acid, and this from sodium nitrate by the action of a small quantity of sulphuric acid.

The following equations represent the chief steps:—

$$\mathrm{NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3},$$
$$\mathrm{2H_2O + 3SO_2 + 2HNO_3 = 3H_2SO_4 + 2NO},$$
$$\mathrm{2NO + O_2 = 2NO_2},$$
$$\mathrm{H_2O + SO_2 + NO_2 = H_2SO_4 + NO}$$

Quantivalence.—The sulphuric radical is bivalent (SO_4''), and acid as well as normal sulphates are known. Acid potassium sulphate, $KHSO_4$, is an illustration of the former, sodium sulphate, Na_2SO_4, of the latter.

Manufacture of Sulphuric Acid.

Chamber Process.—On the large scale, sulphurous anhydride together with nitric acid vapour is carried by means of flues into large leaden chambers, where jets of steam supply the necessary moisture,* and into which air is also passed. The resulting dilute sulphuric acid, which collects

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* In the absence of a sufficient supply of water vapour, a white crystalline substance, *nitro-sulphonic acid*, $\mathrm{SO_2} < \begin{matrix}\mathrm{OH}\\ \mathrm{NO_2}\end{matrix}$ may be produced (sometimes called "chamber crystals"). The manufacturer of sulphuric acid takes steps to ensure the presence of so much water vapour that these crystals are never formed. The following equations represent the formation of nitro-sulphonic acid, and its decomposition by water:—

$$\mathrm{2SO_2 + 3NO_2 + H_2O = 2SO_2} < \begin{matrix}\mathrm{OH}\\ \mathrm{NO_2}\end{matrix} + \mathrm{NO},$$
$$\mathrm{2SO_2} < \begin{matrix}\mathrm{OH}\\ \mathrm{NO_2}\end{matrix} + \mathrm{H_2O = 2H_2SO_4 + NO_2 + NO}$$

on the floor of the chambers, is drawn off, and is concentrated by evaporation in leaden, and finally in glass or platinum, vessels.

Contact Process.—Sulphuric acid is now made in some places on the manufacturing scale by aid of the recently perfected "contact" process. In this process sulphurous anhydride, SO_2, combines directly with oxygen to form sulphuric anhydride, SO_3, when mixed with oxygen and passed through tubes in which the mixture is exposed to a large surface of finely divided metallic platinum in the form of platinized asbestos. The sulphurous anhydride is obtained by roasting iron pyrites and must be purified in a most thorough manner from the last traces of volatile arsenium compounds and from some other volatile compounds present as impurities derived from the pyrites; but it remains mixed with considerable quantities of oxygen and nitrogen from the air drawn into the furnaces in which the pyrites is roasted. The cooled mixture of gases is then brought as thoroughly as possible into contact with platinized asbestos placed in trays in upright iron pipes. To begin with, these pipes are heated in order to start the combination; but they are afterwards exposed to the cooling influence of the external air, the heat given out by the occurrence of the reaction being more than sufficient to maintain the temperature at the point at which the maximum yield of sulphuric anhydride is obtained.

The sulphuric anhydride produced by the reaction is passed into previously prepared 98 per cent. sulphuric acid in which it is rapidly absorbed with formation of pyrosulphuric acid, $H_2S_2O_7$; and the latter is then mixed with the quantity of water necessary to reduce it again to the condition of 98 per cent. sulphuric acid or to sulphuric acid of any required concentration:—

$$H_2SO_4 + SO_3 = H_2S_2O_7;$$
$$H_2S_2O_7 + H_2O = 2H_2SO_4$$

Ferric oxide may be used as the contact substance instead of platinized asbestos.

Other processes.—Sulphuric acid may be obtained by other processes, as by distilling the ferrous sulphate resulting from the natural oxidation of iron pyrites by air; but it is not so made at the present day. Ferrous sulphate was formerly called *green vitriol*, and the distilled product was called *oil of vitriol* in allusion to its consistence and origin.

Purification.—Commercial sulphuric acid, prepared by the chamber process, may contain arsenium compounds, nitrous compounds, and salts (lead sulphate, etc.). Arsenium may be detected by the hydrogen test (p. 197), or the stannous chloride test (p. 201), nitrous compounds by means of powdered ferrous sulphate (which acquires a violet tint if they are present), and salts by observing the residue left on boiling some of the acid to dryness in a crucible in a fume-cupboard. If only nitrous compounds are present, the acid may be purified by heating with about one-half per cent. of ammonium sulphate—water and nitrogen being produced (Pelouze). If arsenium compounds be present, heat with a small quantity of nitric acid (or sodium nitrate), which converts arsenious anhydride, As_4O_6, into arsenic anhydride, As_2O_5, then add ammonium sulphate, and distil, on a sand bath, in a retort containing a few small pieces of quartz, or of platinum wire or foil (to prevent "bumping"—*see* p. 301). The arsenic anhydride remains in the retort (arsenious anhydride would be carried over with the sulphuric acid vapours). The distillation frees the acid from other salts (such as $NaHSO_4$ and $PbSO_4$) which are not volatile. Lead may be detected by adding to the concentrated acid a few drops of hydrochloric acid, or a crystal of sodium chloride; the lead chloride precipitated gives a peculiar pearly opalescence to the liquid.

Pure sulphuric acid, H_2SO_4, has sp. gr. 1·848. The best "oil of vitriol" of commerce, a colourless liquid of oily consistence, has sp. gr. 1·843, and contains about 98 per cent. of hydrogen sulphate. The latter is *Acidum Sulphuricum*, B.P. *Acidum Sulphuricum Dilutum*, B.P. (sp. gr. 1·094) contains about 13½ (13·65) per cent. of hydrogen sulphate. *Acidum Sulphuricum Aromaticum*, B.P. an acid diluted with alcohol and mixed with tincture of ginger and spirit of cinnamon, also contains about 13 per cent. of hydrogen sulphate. Aromatic sulphuric acid may contain sulphovinic acid in varying quantity, dependent upon the internal and external temperature during and subsequent to preparation, the age of the sample, etc. There are some definite compounds of sulphuric acid with water; one of these (H_2SO_4, H_2O) may be obtained in crystals.

Sulphuric anhydride, SO_3, occurs in white crystals which interact with water with great violence, and produce sulphuric acid. As well as by the direct union of sulphurous anhydride and oxygen, it may be made by distilling sulphuric acid with phosphoric anhydride: $H_2SO_4 + P_2O_5 = 2HPO_3 + SO_3$. It unites with sulphuric acid to form "fuming sulphuric acid" or *pyrosulphuric acid*, $H_2S_2O_7$, formerly made at Nordhausen, in Saxony, by distilling partially dried and oxidized ferrous sulphate.

Note.—Sulphuric acid is a most valuable compound to all chemists and manufacturers of chemical substances. By its agency, direct or indirect, a very large number of chemical transformations are effected.

Analytical Reactions of Sulphates.

1. To a solution of a sulphate add solution of a barium salt; a white precipitate of barium sulphate, $BaSO_4$, is produced. Add nitric acid and boil; the precipitate does not dissolve.

This reaction is as highly characteristic of sulphates as it has been stated to be of barium salts (*see* p. 114). The only error likely to be made in its application is that of overlooking the fact that barium nitrate and chloride are less soluble in concentrated nitric (or hydrochloric) acid than in water. On adding the barium salt to an acid liquid, therefore, a white precipitate may be obtained, which is simply barium nitrate (or chloride). The appearance of such a precipitate differs considerably from that of the barium sulphate, but should any doubt exist, water may be added, which will dissolve the nitrate or chloride, but will not affect the sulphate.

2. Mix a fragment of an insoluble sulphate (*e.g.* $BaSO_4$) with potassium or sodium carbonate, or, better, with a mixture of both carbonates, and fuse in a small crucible. Digest the residue, when cold, in water, and filter; the filtrate may be tested for the sulphuric radical.

This is a convenient method of qualitatively analysing insoluble sulphates, such as those of barium and lead.

3. Mix a fragment of an insoluble sulphate with sodium carbonate on a piece of charcoal, taking care that some of the charcoal dust is included in the mixture. Heat the mixture in the blowpipe-flame until it fuses, and, when cold, add a drop of acid; hydrogen sulphide is evolved, recognisable by its odour.

This is another process for the recognition of insoluble sulphates. Other preparations of sulphur, and sulphur itself, give a similar result. It is therefore rather a test for sulphur and its compounds than for sulphates only.

Antidotes.—In cases of poisoning by sulphuric acid, solution of sodium carbonate (common washing soda), magnesia and water, etc., may be administered as antidotes.

THIOSULPHURIC ACID, $H_2S_2O_3$, AND OTHER THIOSULPHATES

The only thiosulphate of much interest in pharmacy is the sodium salt, $Na_2S_2O_3, 5H_2O$ (Sodium Thiosulphate, B.P.). It was formerly known as *sodium hyposulphite*, and is used in photography under the name of "hypo." (True hyposulphites are now known, *e.g.*, $Na_2S_2O_4$.)

Thiosulphates may be regarded as sulphates in which one-fourth of the oxygen has been replaced by sulphur. Thiosulphuric acid has not been isolated.

Preparation of sodium thiosulphate.—Heat together gently, or set aside in a warm place, a mixture of solution of sodium sulphite (Na_2SO_3) and a little powdered sulphur; combination slowly takes place, and sodium thiosulphate is formed. The solution, filtered from excess of sulphur, readily yields crystals. (The solution of sodium sulphite may be made by saturating solution of sodium hydroxide with sulphurous anhydride.) Sodium thiosulphate is obtained on the manufacturing scale by the interaction of sodium sulphate with the calcium thiosulphate formed by the action of atmospheric oxygen and carbonic anhydride on the waste calcium sulphide from the Leblanc soda process.

Use of sodium thiosulphate in quantitative analysis.—In the British Pharmacopœia, sodium thiosulphate is given as a reagent for the quantitative determination of free iodine in volumetric analysis. To a few drops of iodine solution add cold starch mucilage; a deep-blue colour (starch iodide), is produced. To the product add solution of sodium thiosulphate until the blue colour just disappears. This reaction is sufficiently definite and delicate to admit of application for quantitative purposes. It depends on the combination of iodine with half of the sodium of the thiosulphate to form sodium iodide, while sodium tetrathionate, $Na_2S_4O_6$ (from τέτρα, *tetra*, four, and θεῖον, *theion*, sulphur), is formed at the same time.

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

Use of "Hypo" in Photography.—Sodium thiosulphate is largely used in photography to dissolve silver chloride, bromide, or iodide off plates which have been exposed in the camera and developed. Prepare a little silver chloride by adding a chloride (sodium chloride) to a few drops of solution of silver nitrate. Collect the precipitated chloride on a filter, wash, and add a few drops of solution of sodium thiosulphate; the silver salt dissolves, solution of sodium silver thiosulphate being formed. The solution of this thiosulphate has a remarkably sweet taste, sweeter than syrup if the solution is concentrated. Sodium gold thiosulphate has been employed for giving a pleasant tint to photographic prints.

Test.—To solution of a thiosulphate add a few drops of dilute sulphuric or other acid and smell the mixture; thiosulphuric acid is set free, but at once begins to decompose into sulphurous anhydride, recognisable by its odour, free sulphur, and water ($H_2S_2O_3 = SO_2 + S + H_2O$). Another test for a thiosulphate in solution is its power of dissolving silver chloride with production of a more or less sweet liquid.

PERSULPHURIC ACID, $H_2S_2O_8$, AND OTHER PERSULPHATES

Persulphuric anhydride, S_2O_7, was obtained by Berthelot in 1887. It yields a solution in water which probably contains some persulphuric acid but soon decomposes giving oxygen and sulphuric acid.

Salts of persulphuric acid were first prepared by H. Marshall in 1891, potassium persulphate, $K_2S_2O_8$, and ammonium persulphate, $(NH_4)_2S_2O_8$, being obtained by the electrolysis of saturated solutions of potassium sulphate and of ammonium sulphate, respectively, in dilute sulphuric acid. Barium persulphate can be prepared by the interaction of barium hydroxide with a saturated solution of ammonium persulphate and evaporation of the solution *in vacuo.*

The persulphates are of some industrial importance as bleaching and general oxidizing agents, and in the latter capacity they serve a number of purposes in chemical analysis. Their solutions dissolve various metals, such as zinc, magnesium, aluminium, copper, etc., without the evolution of any gas, sulphates being formed: $Zn + K_2S_2O_8 = ZnSO_4 + K_2SO_4$. Potassium persulphate was put upon the market some time ago, under the name "anthion," as a hypo-eliminator in photography, a purpose for which it is, however, quite unsuitable. It is sparingly soluble in water. Ammonium persulphate has also found useful application in photography as a "reducer." Sodium persulphate is obtained by the action of sodium hydroxide on ammonium persulphate, or by the electrolysis of a saturated solution of acid sodium sulphate; under the name "persodine" an aqueous solution of the salt has been introduced into medicine as an aperitive and eupeptic.

Analytical Reactions of Persulphates.—In presence of moisture persulphates gradually decompose with formation of sulphate and evolution of oxygen, $2K_2S_2O_8 + 2H_2O = 4KHSO_4 + O_2$; consequently most solutions, unless freshly prepared from pure persulphate, give a white precipitate on the addition of barium nitrate; pure solutions give a precipitate of sulphate slowly, on boiling.——Hydrochloric acid is decomposed, slowly in the cold but rapidly on warming, with evolution of chlorine, $K_2S_2O_8 + 2HCl = 2KHSO_4 + Cl_2$.——Potassium iodide is similarly decomposed, with liberation of iodine.——Sulphuric acid, on warming, causes decomposition with evolution of oxygen and ozone.——Ferrous sulphate is converted into ferric sulphate, the solution becoming dark reddish brown when hot. $K_2S_2O_8 + 2FeSO_4 = K_2SO_4 + Fe_2(SO_4)_3$.——In solutions which are not too acid, silver nitrate produces a more or less marked black precipitate of the silver salt ($AgHSO_5$) of another sulphur acid (Caro's acid, monopersulphuric acid, H_2SO_5). The precipitate increases in quantity if the sulphuric acid liberated during its formation is neutralized by means of potassium hydroxide.

Sulphur Oxyacids.—The formulæ of the oxyacids of sulphur afford a series that is as useful as the series of compounds of nitrogen and oxygen in illustrating Dalton's law of multiple proportions.

Sulphurous Acid . .	H_2SO_3	Dithionic Acid . .	$H_2S_2O_6$
Sulphuric Acid . .	H_2SO_4	Trithionic Acid . .	$H_2S_3O_6$
Thiosulphuric Acid .	$H_2S_2O_3$	Tetrathionic Acid .	$H_2S_4O_6$
Hyposulphurous Acid	$H_2S_2O_4$	Pentathionic Acid .	$H_2S_5O_6$

Persulphuric Acid, $H_2S_2O_8$
Monopersulphuric Acid, H_2SO_5.

QUESTIONS AND EXERCISES

State the formula and molecular weight of sulphuric acid.—How is it related to other sulphates?—Write a short article on the manufacture of sulphuric acid, giving equations.—How may nitrous compounds be detected in, and eliminated from, sulphuric acid?—State the method for detecting arsenium in sulphuric acid, and explain the process by which it may be removed.—Define sulphates, acid sulphates, and double sulphates.—What percentage of hydrogen sulphate is contained in oil of vitriol?—By what process is sulphuric anhydride obtained from ordinary sulphuric acid?—Explain the reactions which occur in testing for sulphates.—Calculate the weight of sulphuric acid, of 96·8 per cent., necessary for the production of one ton of dry ammonium sulphate. *Ans.*, 1718 lbs.—Name the antidotes in cases of poisoning by sulphuric acid.—Illustrate by an equation the preparation of sodium thiosulphate.—Mention the characteristic reactions of sodium thiosulphate.—Give the names and formulæ of ten acids, each containing hydrogen, sulphur, and oxygen.

CARBONIC ACID [H_2CO_3], and other Carbonates

Occurrence and varieties of Carbon.—Carbon is a constitutent of all living organisms, and the blackening which is observed when plant or animal tissues and the majority of the many products obtained from such tissues are sufficiently strongly heated, is due to the separation of carbon in a more or less pure form. Coke, charcoal, soot, lamp-black, etc., consist of amorphous carbon mixed with varying quantities of mineral or other impurities derived from the materials from which these substances have been formed. When coal or wood is subjected to dry distillation (*see* p. 140) in iron retorts for the preparation of coal-gas, coke, charcoal, etc., water and other volatile products (including marsh gas, carbonic anhydride, and carbonic oxide, all of which contain carbon) are given off in considerable quantity while the greater proportion of the carbon of the coal or wood remains in the retorts.

Bone-black, or *Animal Charcoal,* is the residue obtained on subjecting dried bones to a red heat without access of air. It is a mixture of about 9 parts of mineral with 1 of carbonaceous matter. The operation may be carried out on a small scale by heating a few fragments of bone in a covered porcelain crucible in a fume-cupboard until smoke and vapour are no longer evolved. The mineral matter may be removed and purified animal charcoal obtained as follows:—Boil powdered animal charcoal with a mixture of four times its weight of hydrochloric acid which has been diluted with its own weight of water; filter; again boil the drained residue with half as much of the diluted acid as was previously employed; again filter; wash the residual charcoal with distilled water until the washings give little or no turbidity with solution of silver nitrate; dry the product in a warm place. It should not yield more than 10 per cent. of moisture when dried at a high temperature, nor more than 15 per cent. of ash when thoroughly incinerated. Thirty grains well shaken with 15 ounces of distilled water containing 0·005 per cent. of ordinary commercial caramel (*see* Index) should remove at least four-fifths of the colour from the liquid. (Hodgkin.)

Wood Charcoal (*Carbo Ligni,* B.P.) is wood similarly ignited without access of air. On incineration it should yield not more than 7½ per cent. of ash.

Decolorizing power of Animal Charcoal.—Animal charcoal, in fragments is employed in decolorizing solutions of common brown sugar, for the production of white sugar. Its power, and the nearly equal power of an equivalent quantity ($\frac{1}{10}$th) of the purified variety, may be demonstrated on solution of litmus or logwood as well as on solution of caramel.

Besides these amorphous varieties of carbon there are two crystalline varieties; namely, *plumbago* or *black-lead,* the material employed in making the cores of the so-called "lead" pencils, which crystallizes in hexagonal plates, and *diamond* which crystallizes in forms belonging to the cubic system. Diamond is the hardest substance known. When any form of carbon is burned in oxygen, carbonic anhydride, CO_2, results.

Carbonates are very common in nature, calcium carbonate, $CaCO_3$, being widely distributed as chalk, limestone, and marble. Hydrogen carbonate (true carbonic acid) is not known as a separate substance, but a solution of carbonic anhydride in water appears to contain some of this acid. Such a solution (*see* below) changes the colour of blue litmus-paper, but the change is only temporary, as the carbonic acid decomposes into water and carbonic anhydride when the paper is exposed to the air for a short time.

Carbonic anhydride, CO_2, is a product of the combustion of all carbonaceous matters, and of the respiration of animals and plants. It is a constant constituent of the atmosphere, in which it is present to the extent of about 3 parts in 10,000, and throughout which it is very equally distributed by *diffusion* (*see* p. 17). The process of carbon assimilation in the vegetable kingdom is dependent upon the presence in the air of this small proportion of carbonic anhydride, and it takes place by the aid of chlorophyll, the green colouring matter of plants, under the influence of direct sunlight. The accumulation of carbonic anhydride in confined air, so as to greatly exceed the proportion just mentioned, gives to such air (in crowded rooms, for example) depressing effects; 4 or 5 per cent. rendering the atmosphere poisonous when taken into the blood from the lungs. Carbonic anhydride (or carbonic acid, which is present to some extent at least in all aqueous solutions of carbonic anhydride) may, however, be taken into the stomach with beneficial sedative effects; hence, probably, much of the value of such effervescing liquids as aerated water (often wrongly called soda-water), lemonade, solutions of the various granulated preparations and effervescing powders, and even potash-water and soda-water properly so-called. The gas liquefies on the application of sufficient pressure at temperatures below 31° C., and the liquid solidifies when still further cooled to $-58°$ C. The relative weights of equal volumes of carbonic anhydride, air, and hydrogen, are respectively 21·89, 14·44, and 1. At ordinary temperatures, water dissolves about its own volume of carbonic anhydride, and the weight of the gas dissolved under increased pressure is proportional to the pressure. An average bottle of aërated water* contains about five times the quantity of carbonic anhydride which the water could dissolve without artificial pressure, and when the cork or stopper is removed, about four-fifths of this quantity escapes, while the balance (about equal in volume to the volume of the water) remains dissolved.

The carbonic anhydride used in the manufacture of sodium carbonate (the carbonate most frequently used in medicine and in the arts generally) is obtained by the decomposition of calcium carbonate (*see* p. 87).

Carbonic Oxide, CO.—Heat in a test-tube two or three fragments of potassium ferrocyanide with eight or ten times their weight of sulphuric acid, and as soon as the gas begins to be evolved, remove the test-tube from the flame, as the action, when once set up, proceeds somewhat tumultuously. Ignite the carbonic oxide at the mouth of the tube; it burns with a pale-blue flame, the product of combustion being carbonic anhydride, CO_2. Carbonic oxide may also be obtained from oxalic acid (*see* p. 346).

Carbonic oxide is a direct poison. It is generated whenever coke, charcoal, or coal burns with an insufficient supply of air. Hence the danger of burning charcoal in braziers (otherwise than under chimneys) in the more or less closed apartments of ordinary dwellings.

Phosgen.—Carbonic oxide unites with chlorine in sunlight to form phosgen (φῶς, *phōs*, light, and γεννάω, *gennaō*, I produce), $COCl_2$, a colourless liquid which interacts readily with water, forming hydrochloric acid and carbonic anhydride, $CO + Cl_2 = COCl_2$; $COCl_2 + H_2O = 2HCl + CO_2$.

Analytical Reactions of Carbonates.

1. To a fragment of marble in a test-tube add dilute hydrochloric acid; carbonic anhydride, CO_2, is evolved, and may be conveyed into water or solutions of salts by the usual delivery-tube.

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* Bottled aërated waters yield carbonic anhydride tumultuously when new, and soon become "flat," but yield it less rapidly and more continuously when older, and then retain palate-sharpness longer. Possibly this is due to a solution of true carbonic acid [H_2CO_3] being less unstable than a mere solution of the gas, CO_2.

This is the process usually adopted in preparing carbonic anhydride for experimental purposes. On the large scale, the gas is prepared from chalk or marble and sulphuric acid, frequent stirring promoting its liberation.

2. Pass the gas into lime-water; a white precipitate of calcium carbonate, $CaCO_3$, is produced. Solution of lead subacetate may be used instead of lime-water, and is perhaps even a more delicate reagent.

The evolution of an odourless gas on the addition of an acid to a salt, heat being applied to the mixture if necessary, and the formation of a white precipitate when the gas is passed into lime-water, afford sufficient evidence of the presence of a carbonate. The presence of carbonates in solutions of alkali-metal hydroxides may be detected by the addition of lime-water. Carbonates in presence of sulphites or thiosulphates may be detected by adding acid potassium tartrate, which decomposes carbonates with effervescence, but does not attack sulphites or thiosulphates; or the substance under examination may first be mixed with excess of potassium bichromate, and dilute sulphuric or hydrochloric acid be then added. The evolution of sulphurous anhydride, from the decomposition of any sulphite or thiosulphate, is entirely prevented by the presence of the bichromate (which would immediately oxidize it to sulphuric acid) while the evolution of carbonic anhydride is not interfered with.

3. Blow air from the lungs through a glass tube into lime-water; the presence of carbonic anhydride is at once indicated by the liquid becoming turbid. By passing a considerable quantity of ordinary air through lime-water, a similar effect is produced. A bottle containing lime-water soon becomes internally coated with calcium carbonate owing to absorption of atmospheric carbonic anhydride.

4. Fill a dry test-tube with carbonic anhydride, passing the gas, by means of a delivery-tube, to the bottom of the test-tube. Being rather more than one and a half times as heavy as air (sp. gr. 1·529), it displaces the latter.

Prove the presence of the gas in the test-tube by pouring it slowly, as if a visible liquid, into another test-tube containing lime-water; the characteristic turbidity is obtained on shaking up the lime-water with the air of the tube. In testing for carbonates by bringing the evolved gas into contact with lime-water, the preparation and adaptation of a delivery-tube may often be avoided by pouring the gas from the generating-tube into that containing the lime-water, in the manner just indicated.

5. Pass carbonic anhydride through lime-water until the precipitate at first formed is dissolved. The resulting liquid is a solution of calcium carbonate in carbonic acid water, or probably calcium bicarbonate, $CaH_2(CO_3)_2$. Boil the solution; carbonic anhydride escapes, and the carbonate is again precipitated.

This experiment serves to show how calcium carbonate is kept in solution in ordinary well-waters, imparting to them the property of "hardness," and how the *fur* or stone-like deposit in tea-kettles and boilers is formed. It should here be stated that calcium sulphate also produces hardness, and that calcium carbonate and sulphate with small quantities of magnesium carbonate and sulphate, constitute the hardening constituents of well-waters, a curd (calcium or magnesium oleate) being formed whenever soap is used with such waters. As the formation of this curd indicates the formation from the soap of insoluble substances which are devoid of detergent properties, it is obviously important, in order to avoid waste of soap, that water as free as possible from these hardening constituents should be employed for washing purposes. The hardness produced by the calcium and magnesium carbonates is termed "temporary hardness," because removable by ebullition; that produced by the sulphates "permanent hardness," because unaffected by ebullition. The addition of lime-water, or a mixture of lime and water, removes temporary hardness, $CaH_2(CO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$, and sodium carbonate, "washing-soda," removes both temporary and permanent hardness, in the latter case sodium sulphate remaining in solution. Barium carbonate (powdered witherite) also decomposes calcium and magnesium sulphates, barium sulphate being precipitated and calcium and magnesium carbonates formed; the latter and the carbonates originally present in the water may then be precipitated by ebullition or by the action of lime-water. But the poisonous character of barium salts prevents the use of barium carbonate to purify water for drinking purposes, as by accident or an unforeseen reaction a portion might become dissolved.

6. Add a solution of potassium or sodium carbonate to a magnesium salt; a white precipitate of a basic magnesium carbonate is produced, but the precipitation is not complete. On boiling, light magnesium carbonate (the substance formerly known as *magnesia alba*) is precipitated (*see* p. 131).

Thiocarbonates or *Sulphocarbonates* resemble carbonates in composition, but contain sulphur in place of oxygen.

Thiocarbonic or *Sulphocarbonic anhydride*, CS_2, commonly termed *carbon disulphide* or *bisulphide* (*Carbonis Bisulphidum*, B.P., and *Carbonei Bisulphidum*, U.S.P.), is a highly volatile and inflammable liquid, easily made from its elements. Sp. gr. 1·268 to 1·269; boiling-point, 46° to 47° C. When pure it is almost odourless, but a commercial specimen, or the pure liquid which has been exposed to light for some time, possesses a disagreeable odour due to impurity. Impure specimens may be rendered almost odourless by digestion with lime and then with copper turnings, or by digesting and distilling with mercuric chloride. It often contains dissolved sulphur. It is slightly soluble in water (about 1 in 400) forming a useful antiseptic fluid. Carbon monosulphide, analogous to carbon monoxide (carbonic oxide), is said to have been obtained.

QUESTIONS AND EXERCISES

Explain the action of hydrochloric acid on animal charcoal in the process of purification of the latter.—Name the chief natural carbonates.—What are the formulæ of carbonic acid and carbonic anhydride?—Adduce evidence of the existence of true carbonic acid.—Carbonic anhydride is constantly exhaled from the lungs of animals; why does it not accumulate in the atmosphere?—State the specific gravity of carbonic anhydride.—By what process may carbonic anhydride be obtained for experimental and manufacturing purposes?—Describe the action of carbonic anhydride on potassium or sodium carbonate.—How may carbonic anhydride be detected in expired air?—To what extent is carbonic anhydride heavier than air?—Calculate what quantity of chalk (90 per cent. pure) will be required to furnish the carbonic anhydride necessary to convert one ton of potassium carbonate (containing 83 per cent. of K_2CO_3) into bicarbonate, supposing no gas to be wasted. *Ans.*, 1500 lbs.—Define "hardness" in water.—How may the presence of carbonates be demonstrated?

OXALIC ACID, $H_2C_2O_4,2H_2O$, and other Oxalates

Sources.—Oxalates occur in nature in the juices of some plants, as wood-sorrel, rhubarb, the common dock, and certain lichens; but hydrogen oxalate and other oxalates are all made artificially. The carbon of many organic substances yields oxalic acid when those substances are boiled with nitric acid, and alkali-metal oxalates when they are roasted with a mixture of potassium and sodium hydroxides.

Experimental process.—On the small scale, a mixture of nitric acid 10 parts, loaf-sugar 2 parts, and water 3 parts, quickly yields oxalic acid. Red fumes are at first evolved abundantly, and crystals are deposited on cooling. A more dilute nitric acid, kept warm, acts more slowly, but yields more oxalic acid. The following process is more economical.

Manufacturing process.—On the large scale, sawdust is roasted with caustic soda, the resulting sodium oxalate decomposed by means of slaked lime, with regeneration of caustic soda and formation of calcium oxalate. The latter is digested with sulphuric acid, and the liberated oxalic acid is purified by recrystallization.

Purified oxalic acid.—The acid made from sugar, recrystallized two or three times, is quite pure. Commercial oxalic acid should be mixed with insufficient water for complete solution, and the mixture occasionally shaken. Most of the impurities, remain undissolved, and the saturated aqueous solution on evaporation yields crystals which are nearly pure. Aqueous solutions of oxalic acid slowly decompose under the influence of light and oxygen.

Quantivalence.—The acid radical of the oxalates is bivalent (C_2O_4''). The formula of oxalic acid is frequently written $(COOH)_2$, $2H_2O$. Both normal oxalates ($R'_2C_2O_4$) and acid oxalates ($R'HC_2O_4$) are known.

Salt of sorrel is a crystalline salt intermediate in composition between oxalic acid and acid potassium oxalate, the crystals containing two molecules of water of crystallization ($KHC_2O_4, H_2C_2O_4, 2H_2O$).

Analytical Reactions of Oxalates.

1. To solution of an oxalate (*e.g.*, ammonium oxalate) add solution of calcium chloride; a white precipitate of calcium oxalate, CaC_2O_4, is produced. Add to the precipitate excess of acetic acid; it is insoluble. Add hydrochloric acid; the precipitate dissolves.

The formation of a white precipitate on adding a calcium or barium salt, insoluble in acetic but soluble in hydrochloric or nitric acid, is usually sufficient proof of the presence of an oxalate. It should be noted, however, that in the presence of sulphates, calcium chloride may produce a precipitate of calcium sulphate which is only slightly soluble in acetic, but is readily soluble in hydrochloric, acid. In the known presence of sulphates, oxalate may be tested for by the addition of calcium sulphate to a solution acidulated with acetic acid only.

2. Heat a fragment of an alkali-metal oxalate (potassium oxalate, for example) in a test-tube; decomposition occurs (accompanied by only a slight darkening), carbonic oxide, CO, is liberated, and carbonate of the metal remains. Add dilute hydrochloric acid to the residue; effervescence occurs.

This is a ready test for most ordinary oxalates, soluble or insoluble, and is trustworthy if, on heating the substance, no charring occurs, or not more than gives a grey colour to the residue. Organic metallic salts decompose when heated, and leave a residue of carbonate, but, except in the case of oxalates, the residue is nearly always accompanied by much carbon. Insoluble oxalates and organic salts of such metals as lead and silver are, of course, liable to be reduced to oxide or even to metal by the action of heat. Such oxalates may be decomposed by boiling with solution of sodium carbonate, and the filtered liquid may be tested for oxalate by the calcium chloride test (or by means of calcium sulphate, in acetic acid solution).

Other Analytical Reactions.—Silver nitrate gives, with oxalates, a white precipitate of silver oxalate, $Ag_2C_2O_4$.——Dry oxalates are decomposed when heated with concentrated sulphuric acid, carbonic oxide and carbonic anhydride escaping. If enough oxalate be employed, the gas may be washed with a caustic alkali, which removes the carbonic anhydride, and the carbonic oxide may then be ignited; it will be found to burn with a characteristic bluish flame.——Oxalates, when mixed with water, black manganese oxide (free from carbonates), and sulphuric acid, yield carbonic anhydride, which may be tested by means of lime-water in the usual manner.——Not only such insoluble oxalates as those of lead and silver above referred to, but any ordinary insoluble oxalate, such as that of calcium or magnesium, may be decomposed by prolonged ebullition with solution of sodium carbonate; after filtration the oxalic acid radical will be found in the filtrate as soluble sodium oxalate.

Antidote.—In cases of poisoning by oxalic acid or salt of sorrel, chalk and water may be administered as antidote (with the view of producing insoluble calcium oxalate), emetics and the stomach-pump, or stomach-siphon, being used as soon as possible.

QUESTIONS AND EXERCISES

How are oxalates obtained?—What is the quantivalence of the oxalic radical?—Give the formula of "salt of sorrel."—Mention the chief test for oxalic acid and other soluble oxalates.—By what reactions are insoluble oxalates recognised?—Name the antidote for oxalic acid, and describe its action.

TARTARIC ACID, $H_2C_4H_4O_6$, and other Tartrates

Sources.—Tartrates exist in the juices of many fruits; but it is from that of the grape that our supplies are usually obtained. Grape-juice contains much acid potassium tartrate, $KHC_4H_4O_6$, which is gradually deposited when the juice is fermented, as in making wine; for while acid potassium tartrate is not very soluble in water, it is still less so in spirituous liquids, and hence it crystallizes out as the sugar of the grape-juice is gradually converted into alcohol. It is found, mixed with calcium tartrate, lining the vessels in which wine is kept; and it is from this crude substance, termed *argal* or *argol*, also from the albuminoid yeasty matter or "lees" deposited at the same time, as well as from any tartrate that may remain in the marc left after the juice has been pressed from the grapes, that, by rough recrystallization, "tartar," still containing 6 or 7 per cent. or more of anhydrous calcium tartrate, $CaC_4H_4O_6$, is obtained. From the tartar, tartaric acid and other tartrates are prepared. In old dried grapes (raisins) crystalline masses of tartar and of grape-sugar are frequently met with.

Verjuice, that is, *verd* juice or green juice, is an old name for the very sour juice of unripe green grapes and of crab apples. It contains tartaric, racemic, and malic acids.

Cream of tartar, purified by crystallization (*Potassii Tartras Acidus*, B.P.), occurs as "a gritty white powder, or fragments of cakes crystallized on one surface"; of a pleasant acid taste, soluble in 200 parts of cold and 6 of boiling water, insoluble in alcohol.*

Quantivalence.—The acid radical of the tartrates is bivalent ($C_4H_4O_6''$), and both normal tartrates ($R'_2C_4H_4O_6$) and acid tartrates ($R'HC_4H_4O_6$) are known. Potassium tartrate ($(K_2C_4H_4O_6)_2$, H_2O, and Rochelle Salt, potassium and sodium tartrate, the official *Soda Tartarata*, are illustrations of normal tartrates, while cream of tartar, $KHC_4H_4O_6$, is an example of an acid tartrate. Constitutional formula of tartaric acid: $C_2H_2(OH)_2(COOH)_2$.

Tartaric Acid

Tartaric Acid (*Acidum Tartaricum*, B.P.), is obtained by boiling cream of tartar with water, adding chalk till effervescence ceases, and then calcium chloride so long as a precipitate falls; the two portions of calcium tartrate thus consecutively formed are thoroughly washed, treated with dilute sulphuric acid, the mixture boiled for a short time, the resulting calcium sulphate mostly separated by filtration, the filtrate concentrated by evaporation, any further calcium sulphate that may have deposited removed as before, and evaporation continued until the solution is sufficiently concentrated to crystallize on cooling. The calcium tartrate obtained from nine ounces of cream of tartar requires five ounces (by weight) of sulphuric acid for complete decomposition.

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* A boiling solution of tartar yields a floating crust of minute crystals on cooling—just as milk yields a floating layer of cream; hence the term *cream* of tartar. "It is called *tartar*," says Paracelsus, "because it produces oil, water, tincture, and salt, which burn the patient as tartarus does." *Tartarus* is Latin (Τάρταρος, Tartaros, Greek) for *hell*. The products of its destructive distillation are certainly somewhat irritating in taste and smell; and the "salt" (potassium carbonate) that is left is diuretic and in larger quantities powerfully corrosive.

$$\underset{\substack{\text{Acid potassium}\\ \text{tartrate}}}{2KHC_4H_4O_6} + \underset{\substack{\text{Calcium}\\ \text{carbonate}}}{CaCO_3} = \underset{\substack{\text{Calcium}\\ \text{tartrate}}}{CaC_4H_4O_6} + \underset{\substack{\text{Potassium}\\ \text{tartrate}}}{K_2C_4H_4O_6} + \underset{\text{Water}}{H_2O} + \underset{\substack{\text{Carbonic}\\ \text{anhydride}}}{CO_2}$$

$$\underset{\substack{\text{Potassium}\\ \text{tartrate}}}{K_2C_4H_4O_6} + \underset{\substack{\text{Calcium}\\ \text{chloride}}}{CaCl_2} = \underset{\substack{\text{Calcium}\\ \text{tartrate}}}{CaC_4H_4O_6} + \underset{\substack{\text{Potassium}\\ \text{chloride}}}{2KCl}$$

$$\underset{\substack{\text{Calcium}\\ \text{tartrate}}}{CaC_4H_4O_6} + \underset{\substack{\text{Sulphuric}\\ \text{acid}}}{H_2SO_4} = \underset{\substack{\text{Calcium}\\ \text{sulphate}}}{CaSO_4} + \underset{\substack{\text{Tartaric}\\ \text{acid}}}{H_2C_4H_4O_6}$$

Tartaric acid occurs in commerce in colourless crystals or in finely crystalline powder. It is readily soluble in water and in alcohol. One gramme dissolved in 5 c.c. of water, 2 c.c. of alcohol (90 per cent.) added, and then water sufficient to produce 8 c.c., forms "Solution of Tartaric Acid," B.P. Aqueous solution of tartaric acid is not stable.

Parcels of tartaric acid often contain crystals of a physically isomeric modification (*see* Isomerism). It is termed *paratartaric acid* (*παρὰ*, *para*, beside) or *racemic acid* (*racemus*, a bunch of grapes), and is a combination of ordinary tartaric acid, whose solution rotates a ray of polarized light to the right (dextrotartaric or right-rotating tartaric acid), with lævotartaric or left-rotating tartaric acid, whose solution rotates a polarized ray to the left.* Racemic acid is inactive in this respect (optically inactive), the opposite properties of its constituents neutralizing each other. Racemic acid is less soluble in alcohol than tartaric acid.

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* According to Van 't Hoff and Le Bel, all compounds that cause such rotation contain at least one atom of carbon with which four *different* atoms or radicals are united. Such carbon atoms are termed *asymmetric*.

Potassium Tartrate. (*See* p. 76.)

Sodium Potassium Tartrate. Rochelle Salt.
(*See* p. 91.)

Tartar Emetic. (*See* p. 208.)

Neutralization Weights of Tartaric Acid, Potassium Carbonate, Potassium Bicarbonate, Sodium Carbonate (crystallized), Sodium Bicarbonate, and Ammonium and Magnesium Carbonates are given in the Appendix. In medical practice, effervescing saline draughts are often designedly prescribed to contain a quantity of acid or alkali considerably in excess of the proportions required for exact neutrality.

Effervescent Tartarated Soda Powder (*Pulvis Sodæ Tartaratæ Effervescens,* B.P.) or *Seidlitz Powder* consists of 3 parts of Rochelle salt (120 grains) with 1 part (40 grains) of sodium bicarbonate (the mixture usually wrapped in blue paper) and 1 part (38 grains) of tartaric acid (wrapped in white paper). When administered, one powder is dissolved in a tumbler rather more than half full of water, the other added, and the mixture drunk during effervescence. It may be noted that the quantity of tartaric acid is $2\frac{1}{2}$ grains in excess of that necessary for the formation of a neutral solution of the mixed sodium and potassium tartrates. The effect of this excess of tartaric acid, and of the presence of carbonic acid produced by the interaction, is to give rise to the formation of acid tartrate and of bicarbonate. The presence of this amount of acid salt gives, according to the taste of some persons, agreeable acidity to the draught. The United States' formula (*Pulvis Effervescens Compositus,* U.S.P.) includes rather less tartaric acid, so that only neutral salts are produced, and the formation of the gritty acid potassium tartrate is avoided. "Double" seidlitz powders contain a double dose of Rochelle salt.

Analytical Reactions of Tartrates.

1. To a solution of any neutral tartrate, or of tartaric acid made neutral by addition of solution of caustic soda, add solution of calcium chloride; a white precipitate of calcium tartrate, $CaC_4H_4O_6$, is produced. Collect the pre-

cipitate on a filter, wash, place a small quantity in a test-tube, and add solution of caustic potash: on stirring the mixture the precipitate dissolves. Heat the solution: the calcium tartrate is reprecipitated.

In this reaction a moderate quantity of the calcium chloride solution should be added at once, and the test should be performed without delay, otherwise the calcium tartrate will assume a crystalline character and be with difficulty dissolved by the caustic potash. The latter should be quite free from carbonate.

The solubility of calcium tartrate in cold caustic potash solution enables the analyst to distinguish between tartrates and citrates, otherwise a difficult matter. Calcium citrate is not soluble, or only to a very slight extent, in the alkali. The absence of much ammonium salt must be ensured, calcium citrate, as well as tartrate, being soluble in solutions of ammonium salts.

2. Acidulate a solution of a tartrate with acetic acid, add potassium acetate, and well stir the mixture; a crystalline precipitate of acid potassium tartrate slowly separates.

This reaction is not applicable in testing for very small quantities of tartrates, the acid potassium tartrate being not altogether insoluble. The precipitate being insoluble in alcohol, however, the addition of the latter renders the test much more delicate.

3. To a neutral solution of a tartrate add solution of silver nitrate; a white precipitate of silver tartrate, $Ag_2C_4H_4O_6$, is produced. Boil the mixture; the precipitate blackens owing to the reduction of the silver tartrate to metallic silver. Or, before boiling, add a drop, or less, of solution of ammonia; a mirror will form on the tube—adhering well to the glass if the tube was thoroughly cleansed. When even an insoluble tartrate is placed in a dry tube with a few fragments of silver nitrate, and a drop, or less, of solution of ammonia is added, a mirror-like character is imparted to each fragment of silver salt when the tube is gently rotated some inches above a Bunsen flame.

Other Reactions. — Tartrates heated with concentrated sulphuric acid char immediately, or at least very rapidly. ——Tartaric acid and the soluble tartrates prevent the precipitation of ferric and other hydroxides on the addition of alkalies, solutions of double tartrates being formed (which on evaporation yield liquids that do not crystallize, but, when spread on sheets of glass, dry up to thin transparent plates or scales). The ferric potassio-tartrate (*Ferrum Tartaratum*, B.P. ; *Ferri et Potassii Tartras*, U.S.P.) is a preparation of this kind.——Metallic tartrates decompose when heated, carbon being set free and metallic carbonate (or metal in the case of easily reducible metals) formed, while the gaseous products possess a peculiar, more or less characteristic smell, resembling that of burnt sugar.

QUESTIONS AND EXERCISES

State the origin of tartaric acid and other tartrates, and explain the deposition of argol, crude acid potassium tartrate, during the manufacture of wine.—Give the chemical formula, and the characters, of "purified cream of tartar"?—Mention the formula and quantivalence of the tartaric radical.—Write the formulæ of a number of tartrates.—Give equations illustrating the production of tartaric acid from purified cream of tartar.—By what general process may normal or double tartrates be obtained from acid potassium tartrate?—Give equations representing the reactions.—Enumerate the tests for tartrates, and describe the effects of heat on metallic tartrates.

CITRIC ACID, $H_3C_6H_5O_7$, H_2O, and other Citrates

Sources.—Citric acid (*Acidum Citricum*, B.P.) exists in the juice of the gooseberry, currant, cherry, strawberry, raspberry (*Rubus Idæus*, U.S.P.), and many other fruits, as well as in other parts of plants. The pulp of the fruit of *Tamarindus indica* (*Tamarindus*, B.P.) contains from 1 to 12 per cent. (in addition to 1·5 of tartaric acid, 0·5 of malic acid, and 3 per cent. of acid potassium tartrate). But it is from the lemon or lime that the citric acid of commerce is usually obtained. For this purpose concentrated lemon-juice is exported from Sicily, concentrated bergamot-juice from the Calabrian coast of South Italy, and concentrated lime-juice from the West Indies. The lime-fruit from *Citrus bergamia* is included in the old Pharmacopœia of India.

Citric acid may be prepared from lemon-juice by the following process:—The hot juice should be neutralized by the addition of powdered chalk, the resulting calcium citrate collected on a filter, washed with hot water till the liquor passes from it colourless (by which not only the colouring-matter but the mucilage, sugar, and other constituents of the juice are got rid of), then mixed with cold water, decomposed by means of sulphuric acid, the mixture boiled for half an hour, filtered, the solution evaporated to a density of 1·21, set aside for 24 hours, then poured off from any deposit of crystalline calcium sulphate, further concentrated and set aside to crystallize. If the quantity of calcium citrate to be decomposed is unknown, the sulphuric acid may be added until a little of the supernatant fluid gives, after a minute or two, a precipitate with solution of calcium chloride. The concentrated solution of citric acid generally crystallizes very slowly. Shaken violently, however, in a bottle with a granule or two of solid acid from a previous crystallization, it quickly yields its citric acid in a pulverulent form, and this drained and redissolved in a very small quantity of hot water yields crystals moderately quickly (Warington).

$$\underset{\text{Citric acid}}{2H_3C_6H_5O_7} + \underset{\substack{\text{Calcium}\\ \text{carbonate}}}{3CaCO_3} = \underset{\text{Calcium citrate}}{Ca_3(C_6H_5O_7)_2} + \underset{\text{Water}}{3H_2O} + \underset{\substack{\text{Carbonic}\\ \text{anhydride}}}{3CO_2}$$

$$\underset{\text{Calcium citrate}}{Ca_3(C_6H_5O_7)_2} + \underset{\text{Sulphuric acid}}{3H_2SO_4} = \underset{\text{Citric acid}}{2H_3C_6H_5O_7} + \underset{\text{Calcium sulphate}}{3CaSO_4}$$

Citric acid is now manufactured by the citric fermentation of glucose, which takes place in presence of the fungi *Citromyces Pfefferianus* and *C. glaber*.

The artificial production of citric acid has been accomplished by Grimaux and Adam, who, starting with glycerin, produce certain chloro- and cyano-derivatives and ultimately citric acid itself; it has also been built up by starting with acetone.

Citric acid itself is the only citric compound of much direct importance to the pharmacist. It usually occurs in colourless crystals soluble in half their weight of boiling and in three-fourths of their weight of cold water, less soluble in alcohol and insoluble in ether. A solution of 30 to 40 grains in 1 ounce of water forms a substitute for lemon-juice. Citrates heated with concentrated sulphuric acid to about 215° F. (101·6° C.) evolve carbonic oxide, and at higher temperatures acetone and carbonic anhydride.

Action of heat on citric acid.—Citric acid when slowly heated first loses its water of crystallization; afterwards (347° F., 175° C.) the elements of another molecule of water are evolved and a residue obtained from which ether extracts *aconitic acid*, $H_3C_6H_3O_6$, identical with the aconitic acid (and the acid first termed *equisetic*) in various species of *Aconitum* and *Equisetum*.

Quantivalence.—The acid radical of the citrates is trivalent ($C_6H_5O_7'''$). Three classes of citrates are known, in which one, two, or all three atoms respectively of the replaceable hydrogen atoms of the acid, $H_3C_6H_5O_7$, are replaced by equivalent proportions of metallic radicals. Constitutional formula of citric acid, $C_3H_4(OH)(COOH)_3$.

The official Lemon-juice (*Succus Limonis*, B.P.) is to be freshly expressed from the ripe fruit, to have a specific gravity of 1·030 to 1·040, and to contain 30 to 40 grains of citric acid ($H_3C_6H_5O_7$, H_2O) in 1 fluid ounce. The acidity may be ascertained by adding solution of caustic potash or soda (the concentration of which has been determined previously with pure crystals of citric acid) till red litmus-paper is turned distinctly blue. Before applying this test to commercial specimens of lemon-juice, the absence of notable quantities of sulphuric, hydrochloric, acetic, tartaric, or other acid must be ensured by application of appropriate reagents. (*See* also "Lemon-juice" in Index.)

Lime-juice as imported into Britain contains an average of 7·84 per cent. of citric acid, rarely rising to 10 per cent. and very seldom falling to 7 per cent. Containing but little sugar and mucilage, it requires no addition of alcohol to preserve it. *Lemon-juice* requires about 10 per cent, of proof spirit to prevent fermentation (Conroy).

Neutralization Weights of Citric Acid, Potassium Carbonate, Potassium Bicarbonate, Sodium Carbonate (crystallized), Sodium Bicarbonate, and Ammonium and Magnesium Carbonates are given in the Appendix. In medical practice, effervescing saline draughts are often designedly prescribed to contain a quantity of acid or alkali considerably in excess of the proportions required for exact neutrality.

Analytical Reactions of Citrates.

1. To a dilute solution of any neutral citrate, or of citric acid carefully neutralized by addition of caustic alkali, add solution of calcium chloride and boil; a white precipitate of calcium citrate, $Ca_3(C_6H_5O_7)_2$, is produced. Treat the precipitate as described in the case of calcium tartrate (p. 350); it is not perceptibly dissolved by the caustic potash.

An approximate separation of citrate and tartrate can be effected by means of this reaction. Both radicals are precipitated as calcium salts, and the rapidly washed precipitate is mixed with solution of caustic potash, diluted, and filtered; the filtrate contains the tartrate, which is shown to be present by reprecipitation on boiling. The precipitate still on the filter is washed, dissolved in solution of ammonium chloride, and the solution boiled; the calcium citrate is reprecipitated. The presence of much sugar interferes with this reaction. A dilute solution of a citrate is not precipitated by calcium chloride until the liquid is heated: precipitation from a concentrated solution, also, is not complete without ebullition of the mixture. This reaction is not thoroughly satisfactory, calcium citrate being *slightly* soluble in alkalies, in the solutions of salts produced in the reaction, and, to a very slight extent, even in cold water. It is readily soluble in acetic acid.

2. To a neutral solution of a citrate add solution of silver nitrate; a white precipitate of silver citrate, $Ag_3C_6H_5O_7$, is produced. Boil the mixture; the precipitate does not blacken rapidly, as silver tartrate does, but only after long boiling.

Other Analytical Reactions.—Citric acid forms no precipitate corresponding to acid potassium tartrate.——Lime-water, in excess, gives no precipitate with a dilute solution of citric acid or of a citrate unless the solution is boiled, calcium citrate being slightly soluble in cold but not in hot water; lime-water usually gives precipitates with tartrates in the cold.——Citrates do not char immediately when heated with concentrated sulphuric acid.——Citric acid and citrates prevent the precipitation of iron by alkalies, soluble double compounds being formed. The official Iron and Ammonium Citrate (*Ferri et Ammonii Citras*, B.P.) is a preparation of this kind.——Metallic citrates decompose when heated, carbonates being formed and carbon set free; the odour of the gaseous products is not so characteristic as in the case of tartrates.——According to Cailletet a cold saturated solution of potassium bichromate turns a solution of tartaric acid dark-brown, carbonic anhydride being evolved, while a solution of citric acid only slowly becomes light-brown.

Pusch's test for the detection of tartaric acid in citric acid depends on the well-known difference in the action of sulphuric acid on tartaric acid and on citric acid. It consists in adding to 1 gramme of powdered citric acid in a dry test-tube 10 grammes of pure concentrated (colourless) sulphuric acid, and keeping the part of the tube containing the mixture immersed in boiling water for an hour. The citric acid dissolves with evolution of gas and frothing to form a lemon-coloured liquid, and if the sample be pure this colour undergoes no change within half an hour; but if as much as one-half per cent. of tartaric acid be present, the lemon colour becomes brownish within that time, and in an hour the mixture is red-brown.

The presence of tartaric acid may also be detected by the following method:—Add 1 gramme of citric acid to 1 c.c. of a 10 per cent. solution of ammonium molybdate, and then a few drops of a very dilute solution of hydrogen peroxide; if tartaric acid is present, a fine blue colour appears: in its absence the colour is yellow. (Crismer.)

QUESTIONS AND EXERCISES

What is the source of citric acid?—Describe the preparation of citric acid, giving equations.—Illustrate by formulæ the various classes of tartrates and citrates.—State the average proportion of citric acid in lemon-juice.—What are the tests for citrates?—How are tartrates separated from citrates?

PHOSPHORIC ACID, H_3PO_4, and other Phosphates

Source.—The source of the ordinary phosphates and of phosphorus itself (*Phosphorus*, B.P.) is the normal calcium phosphate, $Ca_3(PO_4)_2$. This is the chief constituent of the bones and teeth of animals, being derived from the plants on which they feed, plants again obtaining it from the soil. Compounds of phosphorus are also met with in the brain, nerves, muscles, blood, saliva, and, according to Kirkes, even in tissues so simple that one must assume that the compounds are necessary constituents of the substance of the primary cell. Phosphates are eliminated from the system both in the urine and in the fæces.

Phosphorus is obtained from bones by the following processes :—The bones are calcined to remove all traces of animal matter. The resulting *bone-earth* is treated with hot and moderately concentrated sulphuric acid, whereby phosphoric acid and calcium sulphate are produced :—

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 2H_3PO_4 + 3CaSO_4$$

The acid fluid strained from the calcium sulphate and concentrated, is mixed with charcoal, coke, or sawdust and dried in an iron pot. At this stage water escapes, and metaphosphoric acid remains :—$H_3PO_4 = HPO_3 + H_2O$. The mixture is then transferred to a fireclay retort and strongly heated ; phosphorus vapour is evolved and is condensed under water while hydrogen and carbonic oxide escape.

$$4HPO_3 + 12C = P_4 + 2H_2 + 12CO$$

The phosphorus is purified by melting under water containing sulphuric acid and potassium bichromate, and is filtered through canvas and cast into sticks.

Properties.—Phosphorus is "a semi-transparent, wax-like solid (in sticks or cakes), which emits white vapours, and is luminous in the dark when exposed to the air. Sp. gr. 1·77. It is soft and flexible at common temperatures, melts at 110° F. (43·3° C.), ignites in the air at a temperature a little above its melting-point, burns with a luminous flame and produces dense white fumes. It is insoluble in water," but soluble in ether, in boiling oil of turpentine, in carbon bisulphide, absolute alcohol, and chloroform. It is soluble in oil which has been previously heated for a short time to about 300° F. (148·8° C.), to expel moisture—1 part in 99 by weight of dried almond-oil constituting Phosphorated Oil (*Oleum Phosphoratum,* B.P.). A mixture of phosphorus with beeswax, lard, and kaolin forms the official Phosphorus Pill (*Pilula Phosphori,* B.P.).

Granulated or pulverulent phosphorus is obtained by placing a quantity of phosphorus under equal parts of alcohol and water in a bottle, standing the bottle in warm water till the phosphorus melts, then inserting the stopper (glass, not cork), and shaking the whole till cold.

Red or "Amorphous" Phosphorus.—Ordinary phosphorus when kept at a temperature of about 450° F. (232·2° C.) in an atmosphere from which air is excluded, becomes red, opaque, and insoluble in liquids in which ordinary phosphorus is soluble. The red modification of phosphorus obtained in this way undergoes oxidation extremely slowly, and only ignites when heated to near 500° F. (260° C.). Though long regarded as amorphous and still known as *amorphous phosphorus,* its structure is really crystalline. It is used in the manufacture of several varieties of matches, and it has the advantage of not emitting the poisonous fumes given off by ordinary phosphorus.

Quantivalence.—Phosphorus is a quinquivalent element, as seen in the pentachloride, PCl_5, and oxychloride, $POCl_3$; but it often exhibits trivalent activity, as seen in the trichloride, PCl_3, and trihydride, PH_3.

Molecular formula.—The vapour density of phosphorus corresponds to the molecular formula, P_4. Phosphorus in the state of vapour thus differs from oxygen, hydrogen, chlorine, etc., by having four atoms in its molecule, whilst these elements have only two.

Zinc phosphide, Zn_3P_2, is included in the U. S. Pharmacopœia.

Phosphoric Acid

The chief use of phosphorus in pharmacy is for the production of Diluted Phosphoric Acid. Phosphorus is boiled with nitric acid and water until it disappears. The solution, evaporated to a small volume to remove nitrous compounds and diluted until the product has a sp. gr. of 1·5, contains about two-thirds (66·3 per cent.) of phosphoric acid, H_3PO_4, and one-third water, and is the *Acidum Phosphoricum Concentratum,* B.P. The latter, diluted so as to contain nearly

14 (13·8) per cent. of phosphoric acid (equivalent to 10 per cent. of phosphoric anhydride, P_2O_5) constitutes the *Acidum Phosphoricum Dilutum,* B.P., a colourless sour liquid of sp. gr. 1·08. If the necessary appliances are at hand, specimens may be prepared as follows:—Three-quarters of an ounce of the *concentrated,* or a quarter of a pint of the *diluted,* phosphoric acid is made by boiling together 103 grains of phosphorus, 1½ fluid ounces of the official nitric acid, and 2 ounces of water in a flask attached to a vertical condenser (or some such arrangement whereby the condensed products are returned to the flask) until the phosphorus has disappeared.

$$\underset{\text{Phosphorus}}{3P_4} + \underset{\text{Nitric acid}}{20HNO_3} + \underset{\text{Water}}{8H_2O} = \underset{\text{Phosphoric acid}}{12H_3PO_4} + \underset{\text{Nitric oxide}}{20NO}$$

The liquid remaining in the flask is then transferred to a dish (preferably of platinum), evaporated down to about half an ounce, and then diluted with the necessary quantity of distilled water.

The use of the water in the earlier part of the process is to moderate the reaction. Hot concentrated nitric acid oxidizes phosphorus with almost explosive rapidity, hence the acid must be diluted in the first instance, and the dilution must be maintained to prevent the acid from becoming too concentrated by loss of water. Time is saved by using concentrated acid, but in that case constant supervision is necessary in order that water may be added, or the temperature otherwise reduced, should the action become too violent. Deficiency of nitric acid must also be avoided, or some phosphorous acid, H_3PO_3, will be formed.

Markoe, also to economize time, modified the process by adding for every ounce of phosphorus 4 or 5 grains of iodine and, drop by drop, 25 or 30 drops of bromine. The iodine and bromine unite with the phosphorus readily, or even with violence that would be explosive if not controlled by the presence of the cold fluids (further cooled, if necessary, by immersing the vessel in cold water). In the course of the reaction it may be assumed that phosphorus iodide and bromide are first formed. These in the presence of water immediately yield hydriodic and hydrobromic acids (HI, HBr) and phosphoric acid. The nitric acid attacks the hydriodic and hydrobromic acids, yielding the lower oxides of nitrogen (which escape as gas), water, and free iodine and bromine. The latter unite with more phosphorus, and the reactions are repeated. This carrying power of a small quantity of iodine or bromine or both would perhaps be indefinitely prolonged if no vapour of these elements or of hydriodic and hydrobromic acids escaped with the gases. The phosphorus having disappeared, excess of nitric acid is mostly got rid of by dropping in clean rags or paper (nitric oxide, carbonic anhydride, and water being formed) and, the last portions, by adding oxalic acid (which even more readily yields similar products). Evaporation to a syrupy consistence finally removes all traces of iodine, bromine, oxalic acid, and moisture. The product is then diluted to any required extent.

Experimental process.—A flask, into the neck of which a funnel is inserted, while a second funnel is inverted so that its mouth rests within the mouth of the first, is an efficient and convenient arrangement of heating and condensing apparatus for this process, especially if the operation be conducted slowly. (*See* fig. 39.)

Solution of phosphoric acid evaporated to a sp. gr. of 1·850 yields a mass of prismatic crystals, H_3PO_4, especially if a crystal or two of the acid from a previous preparation be dropped into the fluid (Cooper). Further evaporated, it leaves a residue which melts at a low red heat, yielding *pyrophosphoric acid*, $H_4P_2O_7$, and finally, *metaphosphoric acid*, HPO_3 (*Glacial Phosphoric Acid*). (Compare p. 381.)

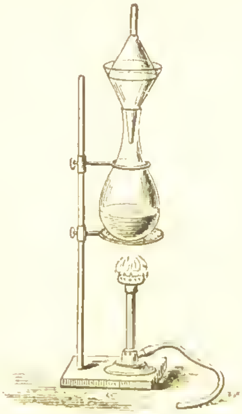

FIG. 39.

A commercial variety of phosphoric acid, containing no large amount of impurity, is prepared by thoroughly digesting a mixture of bone-ash, sulphuric acid, and water; filtering, concentrating, precipitating calcium by means of concentrated sulphuric acid; and heating until sulphuric acid vapours cease to escape. It is also prepared by burning phosphorus so as to obtain phosphoric anhydride, dissolving the latter in water, and boiling with a little nitric acid to oxidize any lower acids of phosphorus and to cause any meta- or pyro-phosphoric acid to take up the elements of water and form ordinary or orthophosphoric acid.

Prepared from bones, phosphoric acid is apt to develop fungoid deposits (Jensen). Prepared from phosphorus, it occasionally contains arsenium in the form of arsenic acid. The latter is detected and removed, together with any traces of platinum or lead, by passing hydrogen sulphide for some time through the warmed acid.

Quantivalence.—The acid radical of the ordinary phosphates, or *orthophosphates*, is trivalent (PO_4'''). By the replacement of all or of a part of the replaceable hydrogen of orthophosphoric acid, H_3PO_4, trimetallic phosphates (M'_3PO_4), dimetallic acid phosphates (M'_2HPO_4), or monometallic acid phosphates ($M'H_2PO_4$), can be obtained. The phosphates met with in nature or used in pharmacy are all orthophosphates.

Crude dry calcium phosphate ground with sulphuric acid yields the very largely used artificial manure termed "superphosphate." It contains acid calcium phosphate, $CaH_4(PO_4)_2, 2H_2O$, and calcium sulphate, $CaSO_4, 2H_2O$.

The rarer pyrophosphates and metaphosphates, as well as the phosphites and hypophosphites, will be mentioned subsequently.

Analytical Reactions of Orthophosphates.

1. To an aqueous solution of a phosphate (*e.g.*, Na_2HPO_4) add solution of magnesium sulphate or chloride with which ammonium chloride and ammonia have been mixed ("magnesia mixture"); a white crystalline precipitate of ammonium magnesium phosphate, NH_4MgPO_4, is produced.

Ammonium chloride is added to prevent the precipitation of magnesium hydroxide. Arsenates, which have close analogy with phosphates, give, with magnesia mixture, a precipitate of analogous composition.

2. To an aqueous solution of a phosphate add solution of silver nitrate; light yellow silver phosphate, Ag_3PO_4, is precipitated—completely, if the mixture be neither acid nor alkaline. To a portion of the precipitate add ammonia; it dissolves. To another portion add nitric acid; it dissolves.

By the first part of this reaction phosphates may be distinguished from their close allies, the arsenates, silver arsenate being brown.

3. To a solution (in a few drops of acid) of a phosphate insoluble in water (*e.g.*, $Ca_3(PO_4)_2$) add an alkali-metal acetate (easily made by adding excess of acetic acid to caustic soda or to ammonia in a test-tube), and then a drop or two of solution of ferric chloride; a yellowish white precipitate of ferric phosphate, $FePO_4$, is produced, insoluble in acetic acid. Too much ferric chloride must not be added, or ferric acetate will be produced, in which the ferric phosphate is to some extent soluble.

To remove the whole of the phosphoric radical from the solution add ferric chloride so long as a precipitate is produced, and boil; ferric phosphate and oxyacetate are precipitated.

To obtain confirmatory evidence of the presence of phosphate in this precipitate (and to separate the phosphoric radical as a phosphate of more characteristic appearance), collect the precipitate on a filter, wash, drop some solution of ammonia on it, then ammonium hydrosulphide, and finally wash with water; black ferrous sulphide remains on the filter, while ammonium phosphate is present in the filtrate. To the filtrate add magnesia mixture and stir well; a granular precipitate of ammonium magnesium phosphate appears.

4. Dissolve a little calcium phosphate (or any other phosphate) in dilute nitric acid, add solution of ammonium molybdate,* and heat gently; a yellow precipitate is produced. This precipitate contains what is somewhat indefinitely termed

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* Molybdenum much resembles lead, hence the name of the metal, from μόλυβδος, *molubdos*, lead. Ammonium molybdate, $(NH_4)_2MoO_4$, is obtained by roasting the native molybdenum sulphide, MoS_2, so as to convert it into molybdic oxide or anhydride, MoO_3, mixing the latter with water, adding ammonia, evaporating and crystallizing. Molybdates having the formulæ M_2MoO_4; $MHMoO_4$; $MHMoO_4$, H_2MoO_4 ($M = 1$ univalent atom of any metal) have been obtained. Commercial ammonium molybdate is commonly the intermediate salt.

phospho-molybdic acid—a compound of molybdic acid and phosphoric acid (about 4 per cent. of H_3PO_4) with ammonia (nearly 7 per cent.).

According to von Juptner tartaric acid, even in large excess, does not prevent the complete precipitation of phosphoric acid by molybdate solution. The addition of tartaric acid to the molybdate solution or to the phosphate is therefore to be recommended, to prevent the contamination of the yellow precipitate with ferric compounds.

Note.—The foregoing two reactions are useful in the analysis of bone-earth, of other earthy phosphates, iron phosphate, and all phosphates insoluble in water. Only arsenates give similar appearances; but the acid solution of these may be decomposed by agitation with sulphurous acid, ebullition, and subsequent treatment with hydrogen sulphide—yellow arsenious sulphide, As_2S_3, being then precipitated.

Other Analytical Reactions of Phosphates.—Solutions of barium and calcium salts give, with aqueous solutions of phosphates, white precipitates of the respective phosphates, $BaHPO_4$, or $Ba_3(PO_4)_2$, and $CaHPO_4$, or $Ca_3(PO_4)_2$, all of which are soluble in acetic and the stronger acids.

QUESTIONS AND EXERCISES

State the direct and indirect sources of phosphorus.—Give equations explanatory of the isolation of phosphorus from its compounds.—Enumerate the properties of phosphorus.—Mention some solvents of phosphorus.—How are the two chief varieties of phosphoric acid made? Describe the precautions to be observed in making this acid.—What are the strengths of the official acids?—Write formulæ illustrative of all classes of orthophosphates.—What is the composition of farmers' "superphosphate," and how is it prepared?—Mention the chief tests for soluble and insoluble phosphates.—By what reactions may phosphates be distinguished from arsenates?

Vanadium, V, 50·8, is a very rare element, and is here mentioned only because of its exceedingly interesting relationship to nitrogen, phosphorus, arsenium, and antimony: along with which it forms a series of five closely allied elements. Discovered, but not isolated, by Sefström, and its compounds investigated by Berzelius, it was obtained in the free state and fully studied by Roscoe.

The subjoined formulæ illustrate the resemblance in composition between some of the compounds of vanadium and those of nitrogen and phosphorus:—

N_2O_5, N_2O_4, N_2O_3, NO, N_2O. V_2O_5, V_2O_4, V_2O_3, VO, V_2O.

Orthophosphates .	R'_3PO_4	Orthovanadates .	R'_3VO_4
Pyrophosphates .	$R'_4P_2O_7$	Pyrovanadates .	$R'_4V_2O_7$
Metaphosphates .	$R'PO_3$	Metavanadates .	$R'VO_3$

Isomorphous Minerals.

Apatite	$3Ca_3(PO_4)_2$, CaF_2
Pyromorphite . . .	$3Pb_3(PO_4)_2$, $PbCl_2$
Mimetesite . . .	$3Pb_3(AsO_4)_2$, $PbCl_2$
Vanadinite	$3Pb_3(VO_4)_2$, $PbCl_2$

BORIC ACID, H_3BO_3, and other Borates

The element boron, like carbon, occurs in the amorphous, graphitoidal, and crystalline conditions. It is a trivalent element yielding halogen compounds, such as the chloride, BCl_3, and fluoride, BF_3. Its atomic weight is 10·85.

The composition of crystallized boric acid (also called *boracic acid*), is expressed by the formula H_3BO_3; but at a temperature of 212° F. (100° C.) this compound loses the elements of water and yields metaboric acid, HBO_2, which, by further loss of water at higher temperatures, becomes boric anhydride, B_2O_3. Metaboric acid exists in the jets of steam (*fumaroles* or *suffioni*) that issue from the earth in some districts of Tuscany, and it collects in the water of the *lagoni* (lagoons or little lakes) formed at the orifices of the steam channels. This acid liquid, evaporated by aid of the waste natural steam, and neutralized by addition of sodium carbonate, yields borax. This salt is usually regarded as sodium pyroborate, $Na_2B_4O_7,10H_2O$, analogous in a sense to potassium bichromate, $K_2Cr_2O_7$. Native borax, or *tincal*, and other borates, are also found in Thibet, Nevada, Peru, Chili, and, abundantly, in California in the Colorado district. Californian borax is represented as forming large portions of the crystalline bed of a dried-up lake. Borax is also made on a large scale by boiling native calcium borate with sodium carbonate. It is sometimes termed sodium biborate. Its official names are *Borax*, B.P., and *Sodii Boras*, U.S.P. It occurs "in transparent colourless crystals, sometimes slightly effloresced, with a weak alkaline reaction; insoluble in alcohol (90 per cent.), soluble in 25 times its weight of cold, and in half its weight of boiling, water."

Fused borax readily dissolves metallic oxides, as will have been noticed already in testing for cobalt and manganese (compare experiment 3, p. 153, and experiment 3, p. 150). Hence, besides its use in medicine, borax is employed as a flux in refining and other metallurgic, and in ceramic, operations; it is also an ingredient in starch glazes. *Glycerinum Boracis*, B.P., is a solution of borax in glycerin. Borax honey formed of 2 parts of borax to 16 of honey, is a very old antiseptic for the mouths of infants troubled by the growth called "thrush," the official preparation (*Mel Boracis*, B.P.) containing, in addition to the foregoing, 1 part of glycerin.

Quantivalence.—The acid radical of the borates is trivalent (BO_3'''); that of the metaborates univalent (BO_2').

Experiment 1.—To a hot concentrated solution of borax add a few drops of sulphuric acid and set aside; on cooling, crystalline scales of boric acid, H_3BO_3 (*Acidum Boricum*, B.P.), are obtained. The acid may be purified by collecting on a filter, slightly washing, drying, digesting in hot alcohol, filtering, and setting aside; pure boric acid is deposited. The acid may also be recrystallized from water. A 2½ per cent. solution in alcohol (90 per cent.) constitutes "Solution of Boric Acid," B.P.

Boric acid occurs in "colourless, pearly, lamellar crystals or irregular masses of crystals; unctuous to the touch; taste feebly acid and bitter, leaving a sweetish after-flavour in the mouth. Soluble in 30 parts of cold water, in 4 of glycerin, in 30 of alcohol (90 per cent.), and in 3 of boiling water. It changes the colour of litmus to wine-red in the cold, a hot saturated solution giving a bright red colour; turmeric paper, moistened with an aqueous solution, even when slightly acidulated with hydrochloric acid, becomes brownish-red on gently drying, and this colour changes to a greenish-black if solution of potassium hydroxide be added. The solution in alcohol burns with a flame tinged with green, especially when the solution is acidulated with sulphuric acid. Boric acid liquefies when warmed, and on careful heating loses 43·6 per cent. of its weight, the product solidifying, on cooling, to a brittle glass-like mass." A solution of boric acid in glycerin is official (*Glycerinum Acidi Borici*, B.P.).

Boric acid is a very weak acid and only slowly decomposes carbonates: a solution of borax possesses a strongly alkaline reaction.

Boric acid is extensively used as an antiseptic in the preservation of foods, especially in the production of "mild-cured" bacon and ham, etc.

Experiment 2.—Mix together 1 part of boric acid, 4 parts of acid potassium tartrate, and 10 to 20 of water; evaporate to a syrupy consistence, spread on plates and set aside for dry scales to form. The resulting substance is far more readily soluble in water than either of its constituents, and is known as *potassium boro-tartrate*, or *soluble cream of tartar*. The Prussian *tartarus boraxatus* differs from the foregoing French variety in containing 1 part of *borax* to 3 of acid potassium tartrate.

Analytical Reactions of Borates.

1. Dip a piece of turmeric paper (paper soaked in tincture of turmeric tubers and dried) into a solution of boric acid; it is coloured brown-red, as by alkalies.

The usual mode of applying this test is as follows:—Add to a solution of any borate a few drops of hydrochloric acid, immerse half of a slip of turmeric paper in the liquid, then dry the paper over a Bunsen flame to develop the brown colour. (Concentrated hydrochloric acid or ferric chloride would produce a somewhat similar change of colour.) Place a drop of caustic soda solution on the browned turmeric paper: a dark green colour is produced.

2. To a fragment of a borate, pyroborate, or metaborate (borax may be used) in a small dish or watch-glass, add a drop of concentrated sulphuric acid and then a little alcohol; warm the mixture and set fire to the alcohol; the resulting flame is tinged green at its edges by the volatilized metaboric acid.

The liquid should be well stirred while burning. Salts of copper and some metallic chlorides produce a somewhat similar colour. The flame-test may also be applied to a small quantity of a mixture of the borate with sulphuric acid on a platinum wire. Glycerin may be used instead of sulphuric acid (Iles), the reaction with borax being, according to Dunstan, the formation of glyceryl borate, $C_3H_5BO_3$, water, and sodium metaborate; the glyceryl borate and water interacting immediately to form boric acid and glycerin. If the borax and the glycerin are both anhydrous no boric acid is formed as the water resulting from the decomposition is immediately volatilized by the heat.

Other Analytical Reactions.—In a moderately concentrated solution of borax, a barium salt produces a white precipitate of barium metaborate, $Ba(BO_2)_2$, soluble in acids and certain salts. Silver nitrate also affords a white precipitate of silver metaborate, $AgBO_2$, soluble in nitric acid and in ammonia. Calcium chloride, if the solution is not too dilute, gives a white precipitate of calcium metaborate, $Ca(BO_2)_2$.

QUESTIONS AND EXERCISES

Illustrate the relations of vanadium to nitrogen and to phosphorus by formulæ of compounds of each element.—Describe the preparation of borax.—Give the formulæ of boric acid, metaboric acid, and borax.—Mention the tests for borates or metaborates.

The foregoing acids and salts comprise those which are commonly employed in ordinary medical or pharmaceutical operations. There are, however, many others which are occasionally used. The chief of these will now be shortly noticed; they are arranged in alphabetical order to facilitate reference.

SALTS OF RARER ACID RADICALS

Benzoic Acid, $HC_7H_5O_2$, and other Benzoates.—Slowly heat a fragment of benzoin (Gum Benjamin) (*Benzoinum*, B.P.)* in a test-tube; benzoic acid (*Acidum Benzoicum*, B.P.) rises in vapour and condenses in small, white, feathery plates and needles on the cool sides of the tube. If the benzoin is first mixed with twice its weight of sand or roughly powdered pumice-stone, and the heat very cautiously applied, the product will be less likely to be burnt, and a larger quantity will be yielded. By repeated sublimation 10 to 15 per cent. may be obtained.

A more economical process is to boil the benzoin with one-fourth its weight of calcium hydroxide, filter, concentrate; decompose the dissolved calcium benzoate by adding hydrochloric acid; collect the precipitated benzoic acid, press between filter-paper, dry, and sublime in a tube or other vessel.

$$\underset{\substack{\text{Benzoic acid}\\\text{(impure)}}}{2HC_7H_5O_2} + \underset{\substack{\text{Calcium}\\\text{hydroxide}}}{Ca(OH)_2} = \underset{\substack{\text{Calcium}\\\text{benzoate}}}{Ca(C_7H_5O_2)_2} + \underset{\text{Water}}{2H_2O}$$

$$\underset{\substack{\text{Calcium}\\\text{benzoate}}}{Ca(C_7H_5O_2)_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid}}}{2HCl} = \underset{\substack{\text{Calcium}\\\text{chloride}}}{CaCl_2} + \underset{\substack{\text{Benzoic acid}\\\text{(pure)}}}{2HC_7H_5O_2}$$

There is always associated with the product a minute quantity of a mixture of volatile oils of agreeable odour, suggesting that of hay, and yielding, according to Jacobsen, methyl benzoate, guaiacol (methoxycatechol), catechol, acetylguaiacol, benzyl benzoate, benzophenone, and benzoylguaiacol.

Benzoic acid is also prepared on a large scale artificially from naphthalin, one of the crystalline by-products in the distillation of coal for gas. The naphthalin is oxidized by nitric acid to naphthalic or phthalic acid:—

$$\underset{\text{Naphthalin}}{C_{10}H_8} + \underset{\text{Oxygen}}{8O} = \underset{\text{Phthalic acid}}{H_2C_8H_4O_4} + \underset{\text{Oxalic acid}}{H_2C_2O_4}$$

The phthalic acid is neutralized by adding lime, and the calcium phthalate is heated with calcium hydroxide for several hours in a covered vessel at a temperature of about 640° F. (337·8° C.). Calcium benzoate and carbonate are formed, and benzoic acid is set free by the action of hydrochloric acid on the mixture.

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* *Sumatra* benzoin (excluding wood) is soluble in ether, and the dissolved substance yields 0·01 per cent. of ash.

$$\underset{\substack{\text{Calcium}\\\text{phthalate}}}{2CaC_8H_4O_4} + \underset{\substack{\text{Calcium}\\\text{hydroxide}}}{Ca(OH)_2} = \underset{\substack{\text{Calcium}\\\text{benzoate}}}{Ca(C_7H_5O_2)_2} + \underset{\substack{\text{Calcium}\\\text{carbonate}}}{2CaCO_3}$$

The crystalline deposit formed when oil of bitter almonds (benzoic aldehyde or benzaldehyde) is exposed to the air is benzoic acid.

$$\underset{\text{Benzaldehyde}}{2C_6H_5COH} + \underset{\text{Oxygen}}{O_2} = \underset{\text{Benzoic acid}}{2C_6H_5COOH \text{ or } 2HC_7H_5O_2}$$

Pure sublimed benzoic acid is also obtained from hippuric acid (p. 372).

Jacobsen has prepared benzoic acid from benzotrichloride (trichloromethylbenzene, $C_6H_5CCl_3$, one of the trichlorotoluenes) by heating with glacial acetic acid and zinc chloride. This acid, if not very highly purified, may give a green colour to the flame when heated on platinum wire with a little copper oxide. In artificial benzoic acid the fragrant volatile oil characteristic of the acid from benzoin is absent.

Properties.—Benzoic acid is slightly soluble in cold water, more so in hot, and readily soluble in alcohol (90 per cent.). It melts at 248° F. (120° C.) and boils at 462° F. (238·8° C.), volatilizing with only a slight residue. Heated with lime it yields benzene. It dissolves in cold sulphuric acid without decomposition, and is deposited again on dilution; the traces of odoriferous and other substances present in the acid obtained from benzoin only slightly colour the fluid, even on warming gently.

Official benzoates.—To a little benzoic acid add a few drops of solution of ammonia or of sodium carbonate; the acid readily dissolves, forming the corresponding benzoate (*Ammonii Benzoas*, B.P., $NH_4C_7H_5O_2$, or *Sodii Benzoas*, B.P., $NaC_7H_5O_2$). With solution of ammonia the reaction is :—

$$\underset{\text{Benzoic acid}}{HC_7H_5O_2} + \underset{\text{Ammonia}}{NH_3} = \underset{\text{Ammonium benzoate}}{NH_4C_7H_5O_2}$$

On evaporating the solution, which is kept slightly alkaline throughout the evaporation by the addition of ammonia, crystals of ammonium benzoate are deposited. Benzoic acid also interacts with other alkaline liquids, forming benzoates.

Test for benzoates.—To a solution of a benzoate add a drop or two of sulphuric or hydrochloric acid; a white crystalline precipitate of benzoic acid separates. To another portion of the solution, carefully made neutral if necessary, add a drop or two of neutral solution of ferric chloride; a reddish precipitate of ferric benzoate results.

Cacodylic Acid $(CH_3)_2AsO{\cdot}OH$.—This is a crystalline acid which is formed on exposure to air of cacodyl oxide, $(CH_3)_4As_2O$ (Cadet's fuming liquid), an exceedingly poisonous and evil-smelling liquid produced by heating a mixture of arsenious anhydride and potassium acetate. Sodium cacodylate, $(CH_3)_2AsO_2Na, 3H_2O$, ferric cacodylate, $[(CH_3)_2AsO_2]_3Fe$, and some other salts are now used in medicine.

A salt somewhat analogous to sodium cacodylate, corresponding to the acid $CH_3AsO(OH)_2$ (methyl-arsonic acid), and represented by the formula $CH_3AsO(ONa)_2, 5H_2O$, has been introduced into medicine under the name *arrhenal.* This salt has been called sodium methyl arsenate, a name which is quite inappropriate as the salt is not an arsenate.

Carminic Acid, $C_{17}H_{18}O_{10}$.—This is the colouring principle (about 10 per cent.) of the dried female cochineal insect, *Coccus Cacti*, (*Coccus*, B.P.). The *carmine* of trade, when unadulterated (*see P. J.*, 1859-60, p. 546) is carminic acid associated with 2 or 3 per cent. of alumina and lime, or, occasionally, of tin oxide or albumen. It should be wholly soluble in solution of ammonia, giving a clear, rich purple liquid. Carmine with French chalk, or starch, constitutes *face rouge* or *animal rouge.*

Merrick tests the relative value of several samples of cochineal or carmine by observing how much solution of potassium permanganate is required to change the colour of a decoction to a faint pink. The silvery coating of cochineal is a wax, *coccerin.*

Cetraric Acid, $H_2C_{18}H_{14}O_8$, is the bitter principle of Iceland moss. In the lichen it is associated with much starch. A fatty acid, lichenstearic acid, is also present.

Cinnamic Acid, C_8H_7COOH.—Benzoic acid is distinguished from an allied acid, cinnamic acid (occurring in Balsams of Peru and Tolu, in Storax, and sometimes in Benzoin), by not yielding benzaldehyde, C_6H_5COH (oil of bitter almonds), when distilled with a mixture of potassium bichromate and sulphuric acid, or when triturated with half its weight of potassium permanganate. Old hard balsam of tolu yields cinnamic acid on boiling with lime and water and precipitating by the addition of hydrochloric acid. Jacobsen makes cinnamic acid artificially by the prolonged interaction of glacial acetic acid and benzodichloride in the presence of zinc chloride.

Cyanic Acid, HCNO, and other Cyanates.—The reducing action of potassium cyanide, KCN (or ferrocyanide, $K_4FeC_6N_6$) on many metallic oxides, is due to the readiness with which it takes up oxygen and forms cyanate, KCNO.

Experiment.—Fuse a few grains of potassium cyanide in a small porcelain crucible and add powdered lead oxide; a globule of metallic lead is at once formed, excess of the oxide converting the whole of the potassium cyanide into potassium cyanate:—$KCN + PbO = KCNO + Pb$.

Potassium cyanate, KCNO, or better, lead cyanate, $Pb(CNO)_2$, treated with ammonium sulphate, yields ammonium cyanate, NH_4CNO; and solution of ammonium cyanate, when evaporated to dryness, leaves a residue of *urea*, CON_2H_4, the most important constituent of urine, and the chief form in which the waste nitrogen is eliminated from the animal system. The process will be more fully described subsequently in connection with urea.

Embelic Acid, $HC_9H_{13}O_2$, appears to be the active principle of the vermifuge fruit of *Embelia Ribes* and *Embelia Robusta* (Embelia, B.P. Add. 1900)—Warden.

Formic Acid, $HCHO_2$. The red ant (*Formica rufa*) and several other insects, when irritated, eject a strongly acid, acrid liquid, which contains formic acid; the acid is also contained in the leaves of the stinging-nettle.

Preparation.—Formic acid may be prepared artificially by heating equal weights of oxalic acid and glycerin to a temperature of from 212° to 220° F. (100° to 104·4° C.) for fifteen hours, and then distilling the mixture with a considerable volume of water. The formic acid, mixed with water, slowly passes over, glycerin being regenerated. The dilute acid may be obtained in a concentrated form by neutralizing with lead carbonate, filtering, evaporating to a small volume, collecting the deposited crystalline lead formate, drying, decomposing in a current of dry hydrogen sulphide, at 212° F. (100° C.), and rectifying the resulting syrupy acid from dry lead formate. It should be fluid at 48° F. (8·9° C.) and boil at 212° F. (100° C.). The following are the chief reactions :—

$$\underset{\text{Glycerin}}{C_3H_5(OH)_3} + \underset{\text{Oxalic acid}}{H_2C_2O_4} = \underset{\text{Glyceryl hydroxyoxalate}}{C_3H_5OHC_2O_4} + \underset{\text{Water}}{2H_2O}$$

$$\underset{\substack{\text{Glyceryl}\\\text{hydroxyoxalate}}}{C_3H_5OHC_2O_4} + \underset{\text{Water}}{2H_2O} = \underset{\text{Glycerin}}{C_3H_5(OH)_3} + \underset{\substack{\text{Formic}\\\text{acid}}}{HCHO_2} + \underset{\substack{\text{Carbonic}\\\text{anhydride}}}{CO_2}$$

Formic Acid may be instructively though not economically prepared by the oxidation of methyl alcohol (wood-spirit), just as acetic acid and valerianic acid are obtained from ethyl alcohol and amyl alcohol respectively—

$$\underset{\text{Methyl alcohol}}{CH_3OH} + \underset{\text{Oxygen}}{2O} = \underset{\text{Formic acid}}{HCOOH} + \underset{\text{Water}}{H_2O}$$

Tests.—Formic acid does not char when heated alone or with sulphuric acid, but splits up into carbonic oxide and water. It is recognised by this property and by its reducing action on salts of gold, platinum, mercury, and silver. It is solid below 32° F. (0° C.).

Gallic Acid.—*See* Tannic Acid.

Hemidesmic Acid.—The supposed active principle of hemidesmus root (*Hemidesmi Radix*, B.P.).

Hippuric Acid, $HC_9H_8NO_3$, is a constituent of human urine (much increased on taking benzoic acid), but is prepared from the urine of the horse (hence the name, from ἵππος, *hippos*, a horse), or better, from that of the cow. To such urine add a little milk of lime, boil for a few minutes, remove precipitated phosphates by filtration, drop in hydrochloric acid until the liquid, after well stirring, is exactly neutral to test-paper, concentrate to about one-eighth the original volume, and add excess of concentrated hydrochloric acid; impure hippuric acid is deposited. From a solution of the impure acid in hot water chlorine removes the colour, and the liquid deposits crystals of pure hippuric acid on cooling.

Tests.—To a solution of a hippurate add neutral solution of ferric chloride; a brown precipitate of ferric hippurate results. Soluble silver and mercurous salts give white precipitates. Heat hippuric acid in a test-tube; it chars, benzoic acid sublimes, and vapours of characteristic odour are evolved; they contain, amongst other products, hydrocyanic acid and a substance smelling somewhat like Tonka bean. The crystalline form of hippuric acid is characteristic; it will be described in connection with the subject of urine.

QUESTIONS AND EXERCISES

Give the preparation, composition, properties, and tests of benzoic acid, employing equations.—What is the nature of carmine?—Name the bitter principle of Iceland "moss."—How is potassium cyanate prepared, how converted into an ammonium salt, and what are the relations of the latter to urea?—Give the formulæ of cyanic acid, ammonium cyanate, and urea.—What is the formula of formic acid?—Describe the artificial production of formic acid.—What is the relation of formic acid to wood-spirit?—State the sources, characters, and tests of hippuric acid.

Hydroferrocyanic Acid, $H_4FeC_6N_6$, or $H_4Fe(CN)_6$, and other Ferrocyanides.—The ferrocyanide of most interest is "Potassium Ferrocyanide," B.P., "yellow prussiate of potash," $K_4FeC_6N_6, 3H_2O$, the formation of which was alluded to in connection with hydrocyanic acid (*see* p. 300). It cannot be regarded as simply a double salt of potassium cyanide with ferrous cyanide ($4KCN, Fe(CN)_2$), its chemical properties being entirely different from those of either of these substances; moreover, unlike potassium cyanide, it is not poisonous. Most of the reactions point to the conclusion that in it iron and cyanogen are intimately united to form the quadrivalent radical appropriately termed *ferrocyanogen* $(FeC_6N_6)''''$. A solution of 1 part of potassium ferrocyanide in 20 of water forms the official "Solution of Potassium Ferrocyanide," B.P.

Tests.—Many of the ferrocyanides are insoluble, and are therefore precipitated when solution of potassium ferrocyanide is added to the salts of the various metals. The precipitates produced in solutions of iron and of cupric salts, being of characteristic colour, are adopted as tests for the presence of these metals or of ferrocyanogen, as the case may be. To a solution of potassium ferrocyanide add a ferric salt; a dark blue precipitate of ferric ferrocyanide, $Fe_4{}^{'''}(FeC_6N_6)_3{}^{''''}$, Prussian blue, is produced. To another portion add solution of a cupric salt; a reddish-brown precipitate of cupric ferrocyanide, $Cu_2FeC_6N_6$ results.

Note.—The ferrocyanogen in potassium ferrocyanide is broken up when the salt is heated with sulphuric acid, *carbonic oxide* being evolved if the acid is concentrated (that is, ordinary oil of vitriol—H_2SO_4 with 2 or 3 per cent. of water), and *hydrocyanic acid* if dilute:—

$$K_4FeC_6N_6, 3H_2O + 3H_2O + 8H_2SO_4 = 4KHSO_4 + FeSO_4 \\ + 3(NH_4)_2SO_4 + 6CO$$

$$2K_4FeC_6N_6 + 6H_2SO_4 = FeK_2FeC_6N_6 + 6KHSO_4 \\ + 6HCN$$

HYDROFERRICYANIC ACID, $H_3FeC_6N_6$, or $H_3Fe(CN)_6$, AND OTHER FERRICYANIDES.—Pass chlorine slowly through a solution of potassium ferrocyanide until the liquid, after frequent shaking, ceases to give a blue precipitate when a minute portion is taken out on the end of a glass rod and brought into contact with a drop of dilute solution of a ferric salt; it now contains "Potassium Ferricyanide" (B.P.), $K_3FeC_6N_6$, "red prussiate of potash," as it is called from the colour of its crystals. Excess of chlorine must be carefully avoided, as cyanogen chloride and other compounds are then formed. Such a result does not ensue if bromine be used instead of chlorine, but this process is less economical.

$$2K_4FeC_6N_6 + Cl_2 = 2KCl + 2K_3FeC_6N_6$$

Note.—The removal of one-half of the potassium from the ferrocyanide is here accompanied by the conversion of the quadrivalent radical ferrocyanogen $(FeC_6N_6)^{''''}$, into the radical *ferricyanogen* $(FeC_6N_6)'''$, which is trivalent. Besides by the action of chlorine, the conversion of potassium ferrocyanide into ferricyanide can be effected by the action of one or other of a variety of oxidizing agents.

Test.—To a solution of potassium ferricyanide add solution of ferrous sulphate; a dark-blue precipitate is produced. This precipitate is ferrous ferricyanide (Turnbull's blue), $Fe_3^{\cdot\cdot}(FeC_6N_6)_2'''$.

$$\underset{\substack{\text{Potassium}\\ \text{ferricyanide}}}{2K_3Fe(CN)_6} + \underset{\substack{\text{Ferrous}\\ \text{sulphate}}}{3FeSO_4} = \underset{\substack{\text{Potassium}\\ \text{sulphate}}}{3K_2SO_4} + \underset{\text{Turnbull's blue}}{Fe_3(FeC_6N_6)_2}$$

A solution of 1 part of potassium ferricyanide in 20 of water forms the official "Solution of Potassium Ferricyanide," B.P.

HYDROFLUORIC ACID, HF, AND OTHER FLUORIDES.—Hydrofluoric acid is chiefly used for etching glass. The operation, performed on the small scale, also constitutes the best test for fluorine, the acid radical of the fluorides.

Experiment and Test.—Coat the convex side of a watch glass (preferably one made of hard glass) with a layer of beeswax, by first heating the glass and then rubbing the wax over it. When the wax is cold, write through it with the point of a pin (or other instrument which is not hard enough to scratch the glass) so as to lay bare some portions of the glass. Place a few grains of powdered fluor-spar (calcium fluoride, CaF_2, the commonest natural fluoride) in a small lead basin (or platinum crucible), add a few drops of sulphuric acid, cover the basin with the prepared glass, waxed side downwards, and very gently warm the bottom of the basin in a fume-cupboard in such a way as not to melt the wax. After a few minutes remove the glass, wash the waxed side by pouring water over it, scrape off most of the wax, then warm the glass and wipe off the remainder; the glass will be found to be etched at the places that were laid bare by the removal of the wax. The hydrofluoric acid liberated by the action of sulphuric acid on the fluor-spar has eaten into or *etched* (from the German *ätzen*, to corrode) the glass.

The calcium fluoride and sulphuric acid yield hydrofluoric acid, thus:—$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$. The hydrofluoric acid gas and the silica of the glass then yield silicic and fluosilicic acids and water, thus:—

$$\underset{\text{Hydrofluoric acid}}{12HF} + \underset{\text{Silica}}{3SiO_2} = \underset{\text{Silicic acid}}{H_4SiO_4} + \underset{\text{Fluosilicic acid}}{2H_2SiF_6} + \underset{\text{Water}}{2H_2O}$$

The silica being removed from the glass, leaves furrows or etched portions.

The aqueous solution of hydrofluoric acid, used by etchers, and commonly termed simply hydrofluoric acid, or "fluoric" acid, is prepared in leaden stills and receivers, and kept in leaden or gutta-percha bottles. Hydrofluoric acid rapidly attacks any substance of which bottles and basins are usually made except lead and gutta-percha. It is also without action on platinum and fluor-spar. It quickly cauterizes the skin, producing a painful, slow-healing sore. A mixture of hydrofluoric acid and ammonium fluoride, known as "white acid," is also used for etching glass.

Experiments by Meslans show that anhydrous hydrogen fluoride has no action on absolute alcohol below 266° F. (130° C.). Above that temperature interaction takes place; and at 410° to 428° F. (210° to 220° C.) about 33 per cent. of the gas is esterified in three hours, and gaseous ethyl fluoride may be collected.

Quantivalence.—Fluorine, like chlorine, bromine, and iodine, is univalent (F').

Fluorine has been isolated by electrolysing hydrofluoric acid. It is a greenish-yellow gas with an irritating odour. It combines with great readiness with all elements except oxygen. By cooling and compressing the gas, Moissan and Dewar have obtained fluorine as a pale-yellowish liquid.

HYPOPHOSPHOROUS ACID, H_3PO_2 or HPH_2O_2, AND OTHER HYPOPHOSPHITES.—Boil together, in a fume-cupboard, two or three grains of phosphorus, three or four grains of calcium hydroxide, and about a quarter of an ounce of water, until hydrogen phosphides are no longer evolved. The volatile products of the interaction are trihydrogen phosphide (or phosphuretted hydrogen), PH_3, and a small quantity of the vapour of a liquid phosphide, P_2H_4. The vapour of the latter ignites spontaneously in contact with air, and imparts to the gaseous mixture the property of spontaneous inflammability. The calcium hydroxide must not be in great excess, or the hypophosphite produced by the interaction will be converted into phosphate as fast as formed. The mixture, filtered, and excess of lime removed by means of carbonic anhydride, yields a solution of calcium hypophosphite, $Ca(PH_2O_2)_2$ (*Calcii Hypophosphis*, B.P.). The salt may be obtained in crystals by evaporation and slow cooling.

$$2P_4 + 6H_2O + 3Ca(OH)_2 = 3Ca(PH_2O_2)_2 + 2PH_3$$

Trihydrogen phosphide or *phosphuretted hydrogen*, PH_3.—The above reaction is the one by which phosphuretted hydrogen is usually prepared. If the gas is to be collected, the phosphorus and water may first be boiled in a flask until a jet of spontaneously inflammable phosphorus vapour escapes, with steam, from the end of the attached delivery-tube. Hot concentrated solution of caustic potash or soda is next very gradually poured into the flask through a funnel-tube previously fitted into the cork, the liquid being kept boiling. Potassium or sodium hypophosphite is formed in solution, while phosphuretted hydrogen is evolved, and if the delivery-tube dip under water may be collected, or allowed to slowly pass up through the water, bubble by bubble, so as to burst into flame spontaneously and form vortex rings of white smoke which rise one after the other into the air and are characteristic of the experiment. A solid hydrogen phosphide, P_4H_2, is known.

Sodium Hypophosphite, $NaPH_2O_2, H_2O$ (*Sodii Hypophosphis*, B.P.) is made by the interaction of solutions of calcium hypophosphite and sodium carbonate, filtering, and evaporating to dryness. $Ca(PH_2O_2)_2 + Na_2CO_3 = 2NaPH_2O_2 + CaCO_3$. It is a white, granular, deliquescent substance. When heated, the water is first evolved, then hydrogen and hydrogen phosphide, and a mixture of sodium pyrophosphate and metaphosphate remains. $5NaPH_2O_2 = Na_4P_2O_7 + NaPO_3 + 2PH_3 + 2H_2$. (Rammelsberg.)

Hypophosphorous Acid, hydrogen hypophosphite (*Acidum Hypophosphorosum Dilutum*, U.S.P.), may be prepared by decomposing the calcium salt by means of oxalic acid, or better, the barium salt by means of sulphuric acid.

Ferri Hypophosphis, $Fe(PH_2O_2)_3$, and *Potassii Hypophosphis*, KPH_2O_2, are included in the United States Pharmacopœia.

Quinine hypophosphite is prepared by dissolving quinine in hypophosphorous acid, or by decomposing quinine sulphate by means of barium hypophosphite. The latter is obtained on boiling excess of pure barium hydroxide with ammonium hypophosphite until all the ammonia has been evolved. The ammonium salt is formed on bringing calcium hypophosphite and ammonium oxalate together in presence of a little ammonia.

The hypophosphites are often used in medicine in the form of syrups (*Syrupus Hypophosphitum*, U.S.P.; *Syrupus Hypophosphitum cum Ferro*, U.S.P.). The term hypophosphite is used in connection with these salts on account of their containing a smaller proportion (ὑπὸ, *hupo*, under) of oxygen than the phosphites (a class of salts which, in turn, contain less oxygen than the phosphates). The prefix *hypo* has similar significance in such words as hyposulphite and hypochlorite.

Tests.—To a solution of calcium or sodium hypophosphite add solution of barium chloride, calcium chloride, or lead acetate; in neither case is a precipitate obtained, whereas soluble phosphates and phosphites yield white precipitates (of barium, calcium, or lead phosphate or phosphite). To other portions of a hypophosphite solution add solutions of silver nitrate and mercuric chloride; precipitates of metallic silver in the one case and of mercurous chloride and then of metallic mercury in the other are produced. (Similar reactions are produced by phosphites.) To another small portion add zinc and dilute sulphuric acid; hydrogen and hydrogen phosphide are evolved (as from phosphites). To a solution of calcium hypophosphite add sufficient oxalic acid to remove the calcium; filter; to the solution of hypophosphorous acid so obtained add solution of cupric sulphate and slowly warm the mixture; a brown precipitate of cuprous hydride, Cu_2H_2, is produced: heat to the boiling-point; hydrogen is evolved and metallic copper is set free. Add a solution of a hypophosphite to a mixture of aqueous solution of ammonium molybdate with solution of sulphurous acid; a blue precipitate results, or in dilute solutions, a blue colour which deepens on standing. Heat a small quantity of a solid hypophosphite on the end of a spatula in a flame, and note the odour of phosphuretted hydrogen and the combustion of this gas. The salt breaks up into pyrophosphate, some metaphosphate, hydrogen, hydrogen phosphide, and water, the official calcium hypophosphite yielding about 80 per cent. of residue.

$$7Ca(PH_2O_2)_2 = 3Ca_2P_2O_7 + Ca(PO_3)_2 + 6PH_3 + H_2O + 4H_2$$

Five grains of calcium hypophosphite, if of good quality, will *almost* decolorize a solution of not less than twelve grains of potassium permanganate, on boiling the mixture for about ten minutes. Five grains of sodium hypophosphite should *almost* decolorize not less than eleven and a half grains of permanganate under similar conditions.

Potassium permanganate, in acid solution, is also reduced by the solution of a phosphite but not by that of an ortho-, meta-, or pyro-phosphate.

QUESTIONS AND EXERCISES

Give the formula of potassium ferrocyanide.—Enumerate the tests for ferrocyanogen.—What are the respective reactions of potassium ferrocyanide with concentrated and dilute sulphuric acid?—Write equations illustrative of the changes effected in potassium ferrocyanide during its conversion into ferricyanide. By what reactions may the presence of a ferricyanide in a solution be demonstrated?—State the difference between Prussian blue and Turnbull's blue.—Describe the source, mode of preparation, chief use of, and test for hydrofluoric acid. What compounds are produced by boiling phosphorus in solutions of alkalies?—Give equations.—How is trihydrogen phosphide prepared?

LACTIC ACID, $HC_3H_5O_3$, AND OTHER LACTATES.—Lactic acid occurs in willow bark (Dott). When milk turns sour, some of its sugar has become converted by the *bacillus acidi lactici*, fed by the nitrogenous matter, into lactic acid (*lac, lactis*). Other saccharine and amylaceous substances also yield lactic acid by fermentation. Neither hydrogen lactate (lactic acid) nor other lactates are much used in Britain.

Preparation.—Calcium lactate and lactic acid may be prepared as follows:—Mix together eight parts of sugar, one of cheese, three of chalk, and fifty of water, and set aside in a warm place (about 80° F.) for two or three weeks; a mass of small crystals of calcium lactate results. Remove these, recrystallize from hot water, decompose by means of sulphuric acid (avoiding excess), digest in alcohol, filter off the calcium sulphate, evaporate the clear solution to a syrup; this residue is ordinary lactic acid (*Acidum Lacticum*, B.P.), sp. gr. 1·21.

A syrup of calcium lactophosphate is official (*Syrupus Calcii Lactophosphatis*, B.P.). It is included in the United States Pharmacopœia, as are also ferrous and strontium lactates (*Ferri Lactas*, U.S.P., $Fe(C_3H_5O_3)_2$, $3H_2O$; and *Strontii Lactas*, U.S.P., $Sr(C_3H_5O_3)_2$, $3H_2O$).

Test.—No single reaction of lactic acid is sufficiently distinctive to be regarded as a test. The crystalline form of calcium lactate, as seen under the microscope, is characteristic. The production of this salt, and the isolation of the syrupy acid itself, are the only means of identification, short of quantitative analysis, on which reliance can be placed. Lactic acid is soluble in water, alcohol, and ether, but almost insoluble in chloroform. It is only slightly coloured by cold sulphuric acid. Warmed with potassium permanganate, it gives the odour of aldehyde.

A variety of lactic acid has been obtained from the juice of flesh; it is termed *sarcolactic* acid (from σὰρξ, σαρκὸς, *sarx, sarcos*, flesh). Unlike lactic acid, it yields a precipitate with solution of cupric sulphate.

MALIC ACID, $C_4H_6O_5$, AND OTHER MALATES (from *malum*, an apple).—The juices of unripe apples, gooseberries, currants, strawberries, grapes, and of rhubarb-stalks, etc., contain malic acid and potassium malate. When isolated, malic acid forms deliquescent prismatic crystals.

Tests.—Calcium malate, $CaC_4H_4O_5$, is soluble in water, hence the aqueous solution of malic acid or other malate is not precipitated by lime-water or calcium chloride; but, on adding alcohol, a white precipitate is produced, owing to the insolubility of calcium malate in that liquid. Malates are precipitated by lead salts; on warming the precipitate of lead malate with acetic acid it dissolves, separating out in acicular crystals on cooling. If the mixture be heated in absence of the acid, the precipitate agglutinates and fuses. Hot concentrated sulphuric acid chars malic acid far less readily than it does nearly all other organic acids.

Asparagin ($C_4H_8N_2O_3$, H_2O).—This proximate principle of plants occurs in many vegetable juices, and doubtless plays a very important part in their nutrition. It is deposited in crystals when the fresh juices of asparagus, marsh-mallow, etc., are rapidly evaporated. It is noticed here because malic acid is readily obtained from it by oxidation, nitrogen being eliminated. When its solution is long boiled it is converted into ammonium aspartate, $NH_4C_4H_6NO_4$. Decomposed by aid of ferments, asparagin, absorbing hydrogen, yields ammonium succinate, $(NH_4)_2C_4H_4O_4$.

MECONIC ACID, $H_2C_7H_2O_7$, $3H_2O$.—Opium contains meconic acid (from *μήκων, mēkōn,* a poppy) partially combined with morphine. To concentrated infusion of opium, nearly neutralized with ammonia, add solution of calcium chloride; crude calcium meconate is precipitated. Wash the precipitate, place it in a small quantity of hot water; add a little hydrochloric acid; the clear liquid (filtered, if necessary) deposits scales of impure meconic acid on cooling.

Tests.—To a solution of meconic acid or other meconate (or to infusion of opium) add a *neutral* solution of ferric chloride; a red solution of ferric meconate is produced. To a portion of the mixture add solution of corrosive sublimate; the red colour is not destroyed: to another portion add hydrochloric acid; the colour is discharged. (These reagents act on ferric thiocyanate, which is of similar tint, with exactly the opposite results.) To another portion add a drop of a dilute acid, and boil; the colour is not discharged. (A solution of ferric acetate, which is of similar colour, *is* decomposed on boiling, giving a colourless fluid and a red precipitate—ferric oxyacetate.)

The normal potassium, sodium, and ammonium meconates are soluble in water, the acid meconates very slightly soluble; he barium, calcium, lead, copper, and silver meconates are nsoluble in water, but soluble in acetic acid.

METAPHOSPHORIC ACID, HPO_3, AND OTHER METAPHOSPHATES.—Prepare phosphoric anhydride, P_2O_5, by burning a small iece of phosphorus in a porcelain crucible placed on a plate and covered by an inverted test-glass, large beaker, or some such vessel. After waiting a few minutes for the phosphoric anhydride to fall, pour a little water on the plate and filter he liquid; the product is a solution of metaphosphoric acid: $P_2O_5 + H_2O = 2HPO_3$.

Tests.—To a solution of metaphosphoric acid add silver ammonio-nitrate, or to a neutral metaphosphate add solution of silver nitrate; a white precipitate of silver metaphosphate, $AgPO_3$, is obtained. This reaction sufficiently distinguishes metaphosphates from the ordinary phosphates or orthophosphates (from *ὀρθός, orthos,* straight), as the common phosphates may, for distinction, be termed (which give, it will be remembered, a *yellow* precipitate with silver nitrate). Another set of salts shortly to be considered, the pyrophosphates, also give a white precipitate with silver nitrate. To the solution of metaphosphoric acid obtained as above or by the action of acetic acid on a metaphosphate, add an aqueous solution of white of egg; coagulation of the albumen ensues. Neither orthophosphoric nor pyrophosphoric acid coagulates albumen. Boil the aqueous solution of metaphosphoric acid for some time; on testing the solution, the acid will be found to have been converted into orthophosphoric acid:—

$$HPO_3 + H_2O = H_3PO_4 \text{ (orthophosphoric acid).}$$

The ordinary medicinal phosphoric acid is made from phosphorus and nitric acid, the liquid being evaporated to a syrupy consistence (or treated as described on p. 359) to remove the last traces of nitric acid. It may contain pyrophosphoric and metaphosphoric acids if the temperature employed be high enough to remove the elements of water:—

$$2H_3PO_4 - H_2O = H_4P_2O_7 \text{ (pyrophosphoric acid).}$$
$$H_3PO_4 - H_2O = HPO_3 \text{ (metaphosphoric acid).}$$

On redilution the metaphosphoric acid only slowly reabsorbs water. If, therefore, on testing the diluted solution metaphosphoric acid be found to be present, the solution should be boiled until conversion into orthophosphoric acid is complete.

NITROUS ACID, HNO_2, AND OTHER NITRITES.—Strongly heat a fragment of potassium or sodium nitrate on a piece of platinum foil; oxygen is evolved, and impure potassium or sodium nitrite remains.

Tests.—Dissolve the residue in water, add a few drops of dilute sulphuric acid, then some dilute solution of potassium iodide, and, lastly, some starch mucilage; the deep-blue "starch iodide" is produced. $2HI + 2HNO_2 = 2H_2O + 2NO + I_2$. Repeat this experiment, using potassium nitrate instead of nitrite; no blue colour is produced. To a solution of a nitrite add solution of ferrous sulphate; a brown coloration is produced. Dissolve a small quantity of a nitrite in concentrated sulphuric acid, and add a few particles of cuprous oxide; an intense violet purple colour is produced.

Tests for Nitrites in Water.—The liberation of iodine from potassium iodide in acid solution by nitrites and not by nitrates is a reaction of considerable value in searching for nitrites in ordinary drinking waters, the occurrence of such salts, except in very deep-seated springs, being held to indicate the presence of nitrogenous organic matter in a state of oxidation or decay. The sulphuric acid used in the operation must be pure, and the potassium iodide free from iodate. If much organic matter is present, however, the nitric acid liberated by the sulphuric acid may be reduced to nitrous acid. It is perhaps best, therefore, to add acetic acid, and distil over 10 or 20 per cent. of the water, and apply the test to this distillate (Fresenius). Very dilute solutions of nitrous acid may thus be distilled without the slightest decomposition.

Sodium Nitrite, $NaNO_2$ (*Sodii Nitris*, B.P.). This salt yields ruddy nitrous fumes on the addition of sulphuric acid. When dissolved in water and tested in a nitrometer, with potassium iodide and dilute sulphuric acid, it should liberate a quantity of nitric oxide, corresponding to not less than 95 per cent. of sodium nitrite.

Other nitrites used in medicine are nitrites of organic radicals. Ethyl nitrite, $C_2H_5NO_2$, or nitrous ether, is the most important constituent of *Spiritus Ætheris Nitrosi*, B.P. A solution of ethyl nitrite in a mixture of absolute alcohol and glycerin is official (*Liquor Ethyl Nitritis*, B.P.). Amyl nitrite, $C_5H_{11}NO_2$, is also official (*Amyl Nitris*, B.P.). Ammonium nitrite, on being heated, yields pure nitrogen :—$NH_4NO_2 = 2H_2O + N_2$.

Determination of nitrous acid in commercial sulphuric acid (Lunge and Swoff's method). 1 c.c. of Griess's reagent is put into each of a pair of Nesslerizing tubes and mixed with 40 c.c. of water and 5 grammes of sodium acetate. To the contents of the first tube 1 c.c. of the suspected acid is added, and to the other, without delay, 1 c.c. of a standard nitrite solution prepared by dissolving 0·0493 gramme of pure sodium nitrite in 100 c.c. of water and diluting 10 c.c. of this to 100 c.c. with pure sulphuric acid. The reddish colours may be compared after any convenient time, but it is best to wait five minutes. Griess's reagent may be prepared as follows :—0·1 gramme of white α-naphthylamine is boiled for fifteen minutes with 100 c.c. of water and mixed with 5 c.c. of glacial acetic acid. The solution is then mixed with 1 gramme of sulphanilic acid dissolved in 100 c.c. of water, and the mixture preserved in a well-corked bottle. If it should become too red, it may be decolorized by shaking it with zinc dust.

Note.—*α-Naphthylamine*, $C_{10}H_7NH_2$, is obtained when α-naphthol is heated for some time either with saturated aqueous ammonia, or with ammonium chloride and caustic alkali under pressure, or by the reduction of nitro-naphthalene. *Sulphanilic acid*, $C_6H_4{\cdot}SO_3H{\cdot}NH_2$, is prepared by heating a mixture of aniline and sulphuric acid containing some pyrosulphuric acid to a temperature of 180° C. for several hours, and pouring into water, when the acid is precipitated in a crystalline form.

OPHELIC ACID, $C_{13}H_{20}O_{10}$.—This is one of the principles to which the herb *Swertia chirata*, or Chiretta (*Chirata*, B.P.), owes its bitterness. It is an amorphous yellow substance.

Another is *Chiratin*, $C_{26}H_{48}O_{15}$, decomposable by hydrochloric acid into *Chiratogenin*, $C_{13}H_{24}O_3$, and ophelic acid (Höhn).

Phosphorous Acid, H_3PO_3 or H_2PHO_3.—A solution containing this acid in small quantity could be obtained by permitting the heavy white fumes which fall from a stick of moist phosphorus on exposure to the air to dissolve in some water placed at the bottom of a wide-mouthed bottle. Or phosphorous oxide, P_4O_6, may first be obtained by gently heating phosphorus in a tube, through which a slow current of air is drawn, condensing the fumes in a U-tube surrounded by a freezing mixture, and then decomposing the oxide by the action of water:—$P_4O_6 + 6H_2O = 4H_3PO_3$. Or chlorine is passed through phosphorus melted under water:—$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$. Having collected some phosphorous acid, apply the various tests already alluded to under *Hypophosphorous Acid*, first carefully neutralizing the phosphorous acid with a caustic alkali.

The soluble phosphites are prepared by neutralizing phosphorous acid with the appropriate alkalies, and the insoluble phosphites by double decomposition.

Associated with phosphorous acid prepared as above stated there is said to be an acid of the formula H_2PO_3, termed *hypophosphoric acid*.

Pyrogallic Acid.—*See* Tannic Acid.

Pyrophosphoric Acid, $H_4P_2O_7$, and other Pyrophosphates. — Heat ordinary sodium phosphate, Na_2HPO_4, $12H_2O$, in a crucible; water of crystallization is first evolved, and anhydrous phosphate, Na_2HPO_4, remains. Further heat to redness; water is again evolved and a new salt is obtained: — $2Na_2HPO_4 = H_2O + Na_4P_2O_7$. The latter is termed sodium pyrophosphate, in allusion to its origin (*πῦρ*, *pūr*, fire). From its solution in water it may be obtained in prismatic crystals, $Na_4P_2O_7$, $10H_2O$. Phosphoric acid itself is similarly affected by heat, yielding pyrophosphoric acid:—$2H_3PO_4 = H_2O + H_4P_2O_7$, though metaphosphoric acid is also formed. Other pyrophosphates are produced similarly, or by double decomposition and precipitation, or by neutralizing pyrophosphoric acid with an oxide, hydroxide, or carbonate. *Ferri Pyrophosphas Solubilis,* and *Sodii Pyrophosphas,* $Na_4P_2O_7$, $10H_2O$, are included in the United States Pharmacopœia.

Tests.—To a solution of a pyrophosphate add solution of silver nitrate; a dense white precipitate of silver pyrophosphate, $Ag_4P_2O_7$, is produced, differing much in appearance from the white gelatinous silver metaphosphate or the yellow orthophosphate. To pyrophosphoric acid, or to a pyrophosphate mixed with acetic acid, add an aqueous solution of albumen (white of egg); no precipitate is formed. Metaphosphoric acid, it will be remembered, gives a white precipitate with albumen. Both pyro- and meta-phosphoric acids give precipitates on adding Tincture of Ferric Chloride.

ACIDS OF PHOSPHORUS

The following acids of phosphorus have now been described:—

Orthophosphoric acid, H_3PO_4
Pyrophosphoric acid, $H_4P_2O_7$
Metaphosphoric acid, HPO_3
Phosphorous acid, H_3PO_3
Hypophosphorous acid, H_3PO_2

The three phosphoric acids (ortho-, pyro-, and meta-) correspond to the higher oxide of phosphorus, P_2O_5, while phosphorous acid corresponds to the lower oxide, P_4O_6. Pyrophosphoric and metaphosphoric acids may be obtained from the ordinary or orthophosphoric acid by the removal of water. Hypophosphorous acid corresponds to a still lower (hypothetical) oxide of phosphorus than P_4O_6. Although three hydrogen atoms are represented in the formulæ of both phosphorous and hypophosphorous acids, the acids behave as dibasic and as monobasic respectively.

QUESTIONS AND EXERCISES

What are the sources of lactic acid?—How is lactic acid usually prepared?—Name some of the plants in which malic acid is found.—Whence is meconic acid derived?—By what process may meconic acid be isolated?—Which is the best test for the meconic radical?—How may meconates be distinguished from thiocyanates?—By what ready method may metaphosphoric acid be obtained for experimental purposes?—Name the tests for metaphosphates.—How may meta- or pyrophosphoric acid be converted into orthophosphoric acid?—Describe the preparation of phosphorous acid.—How are the pyrophosphates prepared?—Give formulæ illustrative of metaphosphates, pyrophosphates, orthophosphates, phosphites, and hypophosphites. — Mention the tests by which meta-, pyro-, and orthophosphates are analytically distinguished.—How are hypophosphites and phosphites detected?

SILICIC ACID, H_4SiO_4, AND OTHER SILICATES.—Silicates of various kinds are among the commonest of minerals. The various *clays* are more or less impure aluminium silicates; the volcanic substance termed *pumice-stone* is a porous aluminium, alkali-metal, and alkaline-earth-metal silicate; the varieties of *felspar* as a rule contain aluminium and alkali-metal silicates or aluminium and alkaline-earth-metal silicates; *meerschaum* is an acid magnesium silicate; the ordinary *sandstones* are chiefly silica; *sand, flint, quartz, agate, chalcedony,* and *opal* are silicic anhydride or *silica*, SiO_2. *Tripoli powder,* a polishing powder now found in many other countries than Tripoli, and consisting of infusorial skeletons, is nearly pure silica. *Bath brick* is a silico-calcareous deposit found in the estuary at Bridgwater and other places. *Tourmalines,* plates of which, cut parallel to the axis of a crystal, are used as polarizers or analysers in microscopy, are all aluminium silicates with varying proportions of iron, copper, manganese, or other silicates. *Asbestos* or *amianth* is a fibrous calcium and magnesium silicate, the length of the fibres varying from less than one inch to five feet. A single silk-like fibre can easily be fused, but even in very small masses, asbestos is infusible in the Bunsen flame, and is incombustible. It is also a bad conductor of heat. It is largely used in packing piston rods and joints, and for steam apparatus generally; as a covering for boilers to prevent loss of heat by radiation; and for so lining ceilings, floors, and other partitions as to render rooms, etc., fireproof.

Artificial acid insoluble silicates are familiar in the form of *glass* and *earthenware*. Common English window-glass (crown glass) is usually calcium, sodium, and aluminium silicate; French glass, calcium and sodium silicate; Bohemian glass, chiefly potassium and calcium silicate; English flint or crystal-glass for ornamental, table, and optical purposes, is mainly potassium and lead silicate. Earthenware is mostly aluminium silicate (clay), with more or less of the easily fusible silicates, namely, those of calcium, sodium, and potassium, and in the commoner forms, iron silicate. The various kinds of *porcelain* (China, Sèvres, Meissen, Berlin, English), *Wedgwood-ware*, and *stoneware* are varieties of earthenware. *Kaolin*, or *China clay*, which is disintegrated *felspar*, is the clay which yields the finest translucent porcelain. When powdered and freed from gritty particles by elutriation, it is official (*Kaolinum*, B.P.). *Crucibles*, *bricks*, and *tiles* are made from different varieties of clay. *Fireclay* contains excess of silica and very small proportions of the fusible silicates, hence its refractory character. *Mortar*, if old, contains a little calcium silicate, but its binding action is due to the soft slaked lime penetrating the minute cavities on the surfaces of adjacent bricks and stones, and then becoming converted into an interlacing or "keying" mass of hard particles of calcium carbonate. The admixed sand which mortar contains, renders the mass porous and so far promotes absorption of carbonic anhydride from the atmosphere, but its proportion should not much exceed two measures to one measure of lime, or, by weight, three of sand to one of good lime. *Portland*, *Roman*, and other "hydraulic" *cements* are calcium silicates with more or less aluminium silicate. *Fuller's earth* (*fullones*, cleansers of cloth) is chiefly silica, but contains combined calcium, magnesium, aluminium, and iron, with a small quantity of potassium. Like the Arab's *tfol*, another earth containing gelatinous silica, Fuller's earth is a powerful absorbent of oils and fats.

Experiment.—Mix a few grains of powdered flint or sand with about five or six times its weight of sodium carbonate and an equal quantity of potassium carbonate, and fuse a little of the mixture on platinum foil in the blowpipe-flame;

the product is a soluble alkali-metal silicate, a *soluble glass* or *water glass*. Boil the foil in water, for a few minutes; filter; to a portion of the filtrate add excess of hydrochloric acid, evaporate the solution to dryness, and again boil the residue in dilute acid; silicon oxide, silicic anhydride, or *silica*, SiO_2, remains as a light, flaky, insoluble powder.

The foregoing operation constitutes the *test* for silicates. By fusion with alkali the silicate is decomposed, and a soluble alkali-metal silicate formed. On addition of acid, silicic acid, H_4SiO_4, is set free, but remains dissolved if the solution is not too concentrated. The heat subsequently applied eliminates water and converts the silicic acid into silica, SiO_2, which is insoluble in water or hydrochloric acid.

The *soluble glass, water glass,* or *glass liquor* of trade may be prepared by fusion, as above; or by boiling up infusorial earth with solution of sodium hydroxide in closed vessels under a pressure of 7 or 8 atmospheres (the proportions of sodium hydroxide, silica, and water in the latter case being about 1, 2, and 5 respectively). *Liquor Sodii Silicatis,* U.S.P., has sp. gr. 1·300 to 1·400.

By the addition of hydrochloric acid to soluble glass, and the removal of the resulting alkali-metal chloride and excess of hydrochloric acid by dialysis (a process to be subsequently described), a pure aqueous solution of silicic acid may be obtained; it readily changes into a gelatinous mass of silicic acid. Possibly some of the natural crystallized varieties of silica may have been obtained from the silicic acid contained in such an aqueous solution, nearly all natural waters yielding a small quantity of silica when evaporated to dryness with hydrochloric acid.

A variety of silicic acid, H_2SiO_3, sometimes termed *dibasic* to distinguish it from the *tetrabasic* acid, H_4SiO_4, results when the aqueous solution of the latter is evaporated *in vacuo.* Various natural silicates correspond to this acid.

Silicon hydride or *siliciuretted hydrogen,* SiH_4, is a spontaneously inflammable gas formed on treating magnesium silicide with hydrochloric acid. It is the analogue of marsh gas or methane, CH_4. A liquid silicon chloride, $SiCl_4$, analogous to carbon tetrachloride, CCl_4, and a gaseous fluoride, SiF_4 are also known. The latter is formed when sulphuric acid acts on a mixture of a fluoride with silica or a silicate. It interacts with water with the production of silicic and fluosilicic acids (*see* p. 375). A carbon silicide, CSi, known as *carborundum* is formed when carbon and silicon are heated together in an electric furnace.

Many other analogies are traceable between the elements silicon and carbon, especially amongst their organic compounds.

Succinic Acid, $H_2C_4H_4O_4$.—Amber (*Succinum*) is a resin usually occurring in association with coal and lignite. From the fact that fragments of coniferous fruit are frequently found in amber, and impressions of bark on its surface, it is considered to have been an exudation from a species of *Pinus* now probably extinct. Heated in a retort, amber yields, first, a sour aqueous liquid containing acetic acid and *succinic acid*; secondly, a volatile liquid known as *oil of amber*, resembling the oil yielded by most resinous substances under similar circumstances; and, thirdly, a pitchy residue allied to asphalt. The succinic acid is a normal constituent of the amber, the acetic acid is produced during distillation. Succinic acid has also been found in wormwood, in several pine-resins, and in certain animal fluids, such as those of hydatid cysts and hydrocele. It is a product of the vital activity of various micro-organisms, and can be formed by these from carbohydrates, from substances allied to carbohydrates, and from albumen. It may be obtained artificially from butyric or stearic acid by oxidation; and from tartaric and malic acids by reduction.

Both normal and acid succinates, $R'_2C_4H_4O_4$ and $R'HC_4H_4O_4$, are known. A potassium hydrogen succinate, $KHC_4H_4O_4$, $H_2C_4H_4O_4$, H_2O, analogous to salt of sorrel, also exists. Soluble succinates give a bulky brown precipitate with neutral ferric chloride (somewhat less voluminous than ferric benzoate); a white precipitate with lead acetate, soluble in excess of either reagent; with silver nitrate a white precipitate after a time; with barium chloride no precipitate at first, but a white precipitate of barium succinate on the addition of ammonia and alcohol. Succinates are distinguished from benzoates by the last-named reaction, and by not yielding a precipitate on the addition of acids (*see* p. 369).

TANNIC ACID, GALLOTANNIC ACID, OR TANNIN. *Digallic acid*, $C_{14}H_{10}O_9$, $2H_2O$.—This is a very common astringent constituent of plants, but is contained in largest quantity in galls (excrescences on the oak, formed by the puncture and deposited ova of an insect). English galls contain from 14 to 28 per cent. and Aleppo galls (*Galla*, B.P.) 25 to 65 per cent. of tannic acid (*Acidum Tannicum*, B.P.).

Myrobalans (*Myrobalanum*, B.P. Add. 1900), the dried immature fruits of *Terminalia Chebula*, the "Chebulic myrobalans" of commerce, may be used in India and the Eastern Colonies instead of galls. The best contain about 30 per cent. of tannin.

Gallotannic acid...$C_6H_2(OH)_3CO{\cdot}O{\cdot}C_6H_2(OH)_2COOH$
Gallic acid (p. 393)...$C_6H_2(OH)_3COOH$

Preparation.—Expose powdered galls (about an ounce is sufficient for the experiment) to a damp atmosphere for two or three days, and afterwards add sufficient ether to form a soft paste. Let this stand in a well-closed vessel for twenty-four hours, then, having quickly enveloped it in a linen cloth, submit it to strong pressure, so as to separate the liquid portion which contains the bulk of the tannic acid in solution. Reduce the pressed cake to powder, mix it with sufficient ether (to which one-sixteenth of its bulk of water has been added) to form again a soft paste, and press this as before. Mix the expressed liquids, and expose the mixture first to spontaneous evaporation and next to gentle heat until it has acquired the consistence of a soft extract; then place it on earthen plates or dishes, and dry it in a hot-air chamber at a temperature not exceeding 212° F. (100° C.).

The resulting tannic acid is a light brownish powder consisting of thin glistening scales, with a characteristic odour, a strongly astringent taste, and an acid reaction; readily soluble in water, and alcohol (90 per cent.), very sparingly soluble in pure ether, though soluble in the ethereal fluid used in the foregoing process (a mixture of ether, water, and alcohol—the latter contained as impurity in the ether.)

The official preparations of tannic acid are *Glycerinum Acidi*

Tannici, Suppositoria Acidi Tannici, and *Trochiscus Acidi Tannici,* B.P.

Reactions of Tannic Acid.

1. To an aqueous solution of tannic acid add aqueous solution of gelatin; a yellowish-white flocculent compound of the two substances is precipitated.

The above reaction also serves to explain the chemical principle involved in *tanning*—the operation of converting skin into leather. In this process the skin is soaked in infusion of oak-bark, the tannic acid of which, uniting with the gelatinous tissues of the skin, yields a compound very well represented by the above precipitate. The outer bark of the oak contains little or no tannic acid, and is commonly shaved off from the pieces of bark which are large enough to handle; useless colouring matter is thus also rejected. Other infusions and extracts besides that of oak-bark (chiefly catechu, sumach, and valonia) are largely used by tanners; if used alone, these act too quickly, and give a harsh, hard, less durable leather. The tannic acid of these preparations is slightly different from that of oak-bark.

2. To an aqueous solution of tannic acid add a neutral solution of a ferric salt; dark bluish-black ferric tannate is slowly precipitated. This is an excellent test for the presence of tannic acid in vegetable infusions. The precipitate is the basis of nearly all black *writing-ink.* Ferrous salts give at first only a slight reaction with tannic acid; but the liquid gradually darkens: characters written with a liquid of this kind, of proper strength, become quite black in a few hours, and are very permanent.

3. To an aqueous solution of tannic acid add solution of tartar-emetic; antimony tannate is precipitated. This reaction and that with gelatin are useful in the quantitative determination of tannic acid in various substances, the separation of the gelatin tannate being much promoted by previously adding some heavy neutral powder, such as barium sulphate, and well stirring while adding the gelatin.

The variety of tannic acid which occurs in oak-bark is said to be a glucoside; that is, like many other substances, it yields glucose (grape-sugar) when boiled with dilute sulphuric or hydrochloric acid, the other product being gallic acid.

Catechu (*Catechu*, B.P.), *Gambier*, or *Terra Japonica*, an extract of *Uncaria Gambier;* as well as the true (or black) *Catechu*, *Cutch*, or *Terra Japonica*, an extract from *Acacia Catechu* (*Catechu Nigrum*, B.P. Add. 1900, and P.I.) and *A. Suma;* the original African (Gambian) Kino, termed by the Mandingo natives *Kano*, from *Pterocarpus erinaceus*, but not now in commerce; *East Indian Kino* (*Kino*, B.P.), from the *Pterocarpus marsupium;* also *Bengal* or *Butea Kino*, from the *Palas* or *Dhak* tree, *Butea frondosa* (*Buteæ Gummi*, Butea Gum, B.P. Add. 1900; *Buteæ gummi vel Kino Bengalensis*, P.I.); Botany Bay or Australian Kinos from various species of *Eucalyptus* or Blue Gum trees (*Kino Eucalypti*, B.P. Add. 1900); and some other vegetable products — contain a variety of tannic acid (*mimotannic acid*), which gives a greenish precipitate with neutral solutions of ferric salts. According to Paul and Kingzett this acid yields, when decomposed, unfermentable sugar, and an acid different from ordinary gallic acid. Catechu and Gambier also contain *catechuic acid* or *catechin*, $C_{21}H_{20}O_9$, a compound occurring in minute colourless acicular crystals and, like mimotannic acid, affording a green precipitate with ferric salts.

The rind of the fruit of the *pomegranate* (*Punica granatum*) (*Granati Cortex*, B.P. and P.I.) contains tannic acid. The astringency of Pomegranate-root Bark is due to a tannic acid (its anthelmintic properties probably to a resinoid matter, or possibly to what Tanret states to be a liquid alkaloid, *pelletierine*, $C_8H_{15}NO$). A tannic acid also probably gives the astringency to logwood (*Hæmatoxyli Lignum*, B.P.). *Rhatany*-root Bark (*Krameriæ Radix*, B.P.) contains about 20 per cent. of tannic acid, its active astringent principle; rhubarb-root about 9 per cent. *Bearberry* leaves (*Uvæ Ursi Folia*, B.P.) owe most of their therapeutic power to about 35 per cent. of tannic acid. (The cause of their influence on the kidneys is not yet traced). They also contain *arbutin*, a crystalline glucoside. *Larch Bark*, the inner bark of *Pinus*

Larix or *Larix Europæa*, contains, according to Stenhouse, a considerable amount of a tannic acid giving olive-green precipitates with ferric salts, and *larixin* and *larixinic acid*, $C_{10}H_{10}O_5$, a somewhat bitter substance. *Areca nuts* or *Betel nuts*, from the Areca Palm (*Areca Catechu*), besides the alkaloid *arekane* (Bombelon), contain a very active alkaloid, *arecoline*, $C_8H_{13}NO_2$ (Jahns), said to be the vermifugal principle; *arecaine*, an inert alkaloid (Jahns), and according to Flückiger and Hanbury, about 16 per cent. of "tannic matter." *Betel* is also the name given to the leaves of *Piper Betle* (*Betel*, B.P. Add. 1900). It contains volatile oils (Kemp), one constituent of which, *chavicol* (Eykman), appears to be characteristic. A mixture of the nuts and leaves with a little lime, known, shortly, as "Betel," is universally used as a stimulating and exhilarating masticatory by the natives in the East, meeting, apparently, some widespread physiological demand. The leaves of *Pan* (Hind.) are also used in various other ways as a common household drug The extract of the fruit of *Gob* or *Diospyros embryopteris* (*Diospyri Fructus*, P.I.) is a powerful astringent containing tannic acid. The rhizome of *Geranium maculatum*, *Spotted Cranesbill*, or *Alum-root*, and the leaves and stalks of *Somac*, *Sumach*, or *Shumac* (*Rhus*, various species) contain both tannic and gallic acids. The fruit of sumach (*Rhus glabra*, U.S.P.) contains tannic and malic acids. *Poison Ivy* or *Poison Oak* (*Rhus toxicodendron*, U.S.P.) contains poisonous toxicodendric acid especially in spring. The principal constituent of the root-bark of *high blackberry* (*Rubus*, U.S.P.) is tannic acid. *Acaciæ Cortex*, Acacia Bark (B.P. Add. 1900), or *Bobool*, resembles oak-bark in containing tannic acid.

Gallic Acid, $C_7H_6O_5,H_2O$ (p. 390) (*Acidum Gallicum*, B.P.), occurs in small quantity in oak-galls and other vegetable substances, but is always prepared from tannic acid. Gallic acid forms slender acicular, fawn-coloured crystals, soluble in 100 parts of cold or 3 of boiling water, freely soluble in alcohol, sparingly in ether.

Boil one part of coarsely powdered galls with four fluid parts of dilute sulphuric acid for half an hour; strain through calico while hot; collect the crystals that are deposited on cooling, and purify these by treatment with animal charcoal and by repeated crystallization.

Tests.—To an aqueous solution of gallic acid add a neutral solution of a ferric salt; a bluish-black precipitate of ferric gallate is produced, similar in appearance to ferric tannate. Ferrous salts are also blackened by gallic acid. To more of the solution add an aqueous solution of gelatin; no precipitate is formed. By the latter test gallic acid is distinguished from tannic acid.

Pyrogallic acid or *pyrogallol,* $C_6H_3(OH)_3$.—This substance sublimes in light feathery crystals when gallic acid is heated. Or it may be formed by heating gallic acid with 3 or 4 times its weight of glycerin to a temperature of 190° or 200° C. for a short time, until carbonic anhydride is no longer evolved. Longer heating at a lower temperature is not equally effective, and below 100° C. probably no pyrogallol is produced (Thorpe). To an aqueous solution add a neutral solution of a ferric salt; a red colour is produced. To another portion add a ferrous salt; a deep-blue colour results.

Pyrogallol, syn. pyrogallic acid, is officially recognised as a reagent in B.P. Add. 1900.

Test for the three acids, tannic, gallic, and pyrogallic.—To three separate small quantities of milk of lime in test-tubes add, respectively, tannic, gallic, and pyrogallic acids; the first slowly turns brown, the second more rapidly, while the pyrogallic mixture at once assumes a beautiful purplish-red colour changing to brown. These reactions are characteristic; they are accompanied by absorption of oxygen from the air.

Use of Pyrogallol in Gas-analysis.—A mixture of pyrogallol and solution of caustic potash absorbs oxygen with such rapidity and completeness that concentrated solutions of each, passed up successively by means of a pipette into a graduated tube containing air or other gas, over mercury, form an excellent means of determining free oxygen. The value of this method may be proved roughly by pouring a small quantity of each solution into a bottle, immediately and firmly closing its mouth with a cork, thoroughly shaking the bottle, and then removing the cork under water: the water rushes in and occupies about one-fifth of the previous volume of air, indicating that the atmosphere contains one-fifth of its bulk of oxygen. The small quantity of carbonic anhydride present in the air is also absorbed by the alkaline liquid; in delicate experiments this should first be removed by means of the caustic alkali and the pyrogallol then be added.

Thiocyanic Acid, HSCN, and other Thiocyanates.—Boil together sulphur and solution of potassium cyanide; solution of potassium thiocyanate, KSCN, is formed. Warm the liquid, add hydrochloric acid till it faintly reddens litmus-paper, and filter; any potassium sulphide is thus decomposed, and the solution may then be used for the following reactions. The salt readily crystallizes.

Tests.—To a small portion of the solution add ferric chloride; a deep blood-red solution containing ferric thiocyanate is formed. (Solutions of pure ferrous salts are not coloured by thiocyanates.) To a portion of the red liquid add a little hydrochloric acid; the colour is not discharged (ferric meconate, a salt of similar tint, is decolorized by hydrochloric acid). In the acid liquid place a fragment or two of zinc; hydrogen sulphide is evolved, and the red colour disappears.

To another portion of the ferric thiocyanate add solution of mercuric chloride; the colour is at once discharged. (Ferric meconate is unaffected by mercuric chloride.) The reaction with ferric salts is the best test for the presence of a hiocyanate; and indirectly is also a good test for the presence of hydrocyanic acid or other cyanide (*see* p. 301). Red ferric acetate solution is decomposed by ebullition. Neither the ferric acetate nor the meconate yields its colour to ether; but, on shaking ferric thiocyanate solution with ether, the latter takes up the thiocyanate and becomes of a purple colour.

To a solution of a thiocyanate add solution of mercuric nitrate; mercuric thiocyanate is precipitated as a white powder.

Pharaoh's Serpents.—Mercuric thiocyanate, thoroughly washed and made up into little cones, forms the toy termed Pharaoh's serpent. It readily burns when ignited, the chief product being a light solid matter (mellon, $C_6H_3N_9$, and melam, $C_6H_9N_{11}$), which issues from the cone in a snake-like coil of extraordinary length. The other products are mercuric sulphide (of which part remains in the residue and part is volatilized), nitrogen, sulphurous anhydride, carbonic anhydride, and vapour of metallic mercury.

The thiocyanic radical (SCN) is termed thiocyanogen. The thiocyanates were formerly called *sulphocyanides*. Saliva contains thiocyanates.

URIC ACID, $C_5H_4N_4O_3$, AND OTHER URATES.—Acidulate a few ounces of human urine with hydrochloric acid and set aside for twenty-four hours; a few minute crystals of uric acid will be found adhering to the sides and bottom of the vessel and floating on the surface of the liquid.

Microscopical Test.—Place some of the floating particles on a slip of glass, and examine them under a powerful lens or a microscope; the chief portion will be found in the form of more or less square, yellowish, semi-transparent crystals, two of the sides of which are even, and two very jagged; but other forms are common. (*See* the lithographs in the section on Urinary Sediments.)

Chemical Test.—Collect more of the deposit, place in a watch-glass or small white evaporating-dish, remove adherent moisture by means of filter-paper, add a drop or two of concentrated nitric acid, and evaporate to dryness; the residue will be red. When the dish is cold, add a drop of solution of ammonia; a purplish-crimson colour results. The colour is deepened on the addition of a drop of solution of caustic potash.

Notes.—Uric acid (or lithic acid) and sodium, potassium, calcium, and ammonium urates (or lithates) are common constituents of animal excretions. Human urine contains about one part of urate (usually sodium urate) in 1000. When more than this is present, the urate is often deposited as a sediment in the excreted urine, either at once, or after standing a short time. Uric acid or other urate is also occasionally deposited before leaving the bladder, and, slowly accumulating there, forms a common variety of urinary calculus.——Some urates are not definitely crystalline; but, when treated with dilute nitric acid or a drop of solution of caustic potash and then a drop or two of acetic acid, microscopic crystals of uric acid are usually formed. ——All urates yield the crimson colour when treated as above described. This colour is due to a definite substance, *murexid*, $C_8H_8N_6O_6$ (from *murex*, a shell-fish of similar tint, from which the ancient and highly valued purple dye seems to have been prepared), and the test is known as the *murexid* test. The formation of murexid is due to the action of ammonia on *alloxan*, $C_4H_2N_2O_4,4H_2O$, and other white crystalline products of the oxidation of uric acid by nitric acid. Murexid is a good dye; it may be prepared from *guano* (the excrement of sea-fowl), which contains a large quantity of ammonium urate.——The excrement of the serpent is almost pure ammonium urate.

Uric acid and the urates will again be alluded to in connection with the subject of morbid urine.

Constitution of Uric Acid.—The physiological and pathological importance of uric acid has obtained for it great attention from chemists. For accounts of what has been done in recent years towards elucidating its constitution, students of organic chemistry may consult the *Pharmaceutical Journal*, 3rd Series, vol. xiv., p. 771; vol. xv., pp. 119 and 411; and vol. xviii., p. 69. (*See* formula on p. 630).

VALERIANIC ACID (OR VALERIC ACID), $HC_5H_9O_2$, AND OTHER VALERIANATES. In a test-tube place a few drops of amyl alcohol (fusel-oil, which is impure amyl alcohol, may be used) with a little dilute sulphuric acid and a grain or two of potassium bichromate, cork the tube, set aside for a few hours, and then heat the mixture; valerianic acid, of characteristic valerian-like odour, is evolved.

Valerianic acid occurs in valerian-root in association with the essential oil from which it is apparently derived (*see* p. 516), but is usually prepared artificially, by the foregoing process, from amyl alcohol, to which it bears the same relation that acetic acid does to common alcohol :—

$$C_2H_5OH + 2O = HC_2H_3O_2 + H_2O$$
$$C_5H_{11}OH + 2O = HC_5H_9O_2 + H_2O$$

Sodium Valerianate, $NaC_5H_9O_2$, is prepared from the valerianic acid and amyl valerianate obtained on distilling a mixture of amyl alcohol, sulphuric acid, potassium bichromate, and water. The mixture should stand for several hours before heat is applied.

$$\underset{\text{Amyl alcohol}}{C_5H_{11}OH} + \underset{\text{Oxygen}}{2O} = \underset{\text{Valerianic acid}}{HC_5H_9O_2} + \underset{\text{Water}}{H_2O}$$

$$\underset{\text{Amyl alcohol}}{2C_5H_{11}OH} + \underset{\text{Oxygen}}{2O} = \underset{\text{Amyl valerianate}}{C_5H_{11}C_5H_9O_2} + \underset{\text{Water}}{2H_2O}$$

The distillate is saturated with caustic soda, which not only yields sodium valerianate with the free valerianic acid, but also decomposes the amyl valerianate produced at the same time, more sodium valerianate being formed and some amyl alcohol set free, according to the following equations :—

$$\underset{\text{Valerianic acid}}{HC_5H_9O_2} + \underset{\text{Caustic soda}}{NaOH} = \underset{\text{Sodium valerianate}}{NaC_5H_9O_2} + \underset{\text{Water}}{H_2O}$$

$$\underset{\text{Amyl valerianate}}{C_5H_{11}C_5H_9O_2} + \underset{\text{Caustic soda}}{NaOH} = \underset{\text{Sodium valerianate}}{NaC_5H_9O_2} + \underset{\text{Amyl alcohol}}{C_5H_{11}OH}$$

From the solution of sodium valerianate (which should be made neutral to test-paper by careful addition of caustic soda solution) the solid white salt is obtained by evaporation to dryness and cautious fusion of the residue. The mass obtained on cooling should be broken up and kept in a well-closed bottle. It should be entirely soluble in alcohol.

Other Valerianates, as zinc valerianate, $Zn(C_5H_9O_2)_2$ (*Zinci Valerianas*, B.P.), and ferric valerianate, $Fe(C_5H_9O_2)_3$ (*Ferri Valerianas*, U.S.P.), may be made by the interaction of sodium or other valerianate and the sulphate or other salt of the metal the valerianate of which is desired, the new valerianate either precipitating or crystallizing out. A hot solution of zinc sulphate ($5\frac{3}{4}$ parts) and sodium valerianate (5 parts) in water (40 parts) gives a crop of crystals of zinc valerianate on cooling. *Ammonii Valerianas,* U.S.P., in white lamellar crystals, results when dry ammonia gas is passed into valerianic acid.

Tests.—Heated with dilute sulphuric acid valerianates of the metals give a highly characteristic smell (valerianic acid).

Note.—Of the four possible varieties of valerianates, the foregoing are the ordinary or *iso-valerianates,* the constitutional formula for the acid being $(CH_3)_2 = CH - CH_2 - COOH$. *See* the Acetic Series of Acids in the Section on Organic Chemistry.

The amyl alcohol ($C_5H_{11}OH$) from which valerianates are prepared may contain the next lower member of the homologous series of alcohols, *butyl alcohol,* C_4H_9OH. This alcohol, during the oxidation, will be converted into *butyric acid,* $HC_4H_7O_2$, the next lower homologue of valerianic acid, $HC_5H_9O_2$, and hence the various valerianates may be contaminated by some *butyrates.* These are detected by distillation with dilute sulphuric acid and addition of solution of cupric acetate to the distillate, which at once becomes turbid if butyric acid be present. In this reaction valerianic acid and butyric acid are produced by interaction of the valerianate and butyrate and the sulphuric acid, and they distil over on the application of heat. On the addition of cupric acetate, $Cu(C_2H_3O_2)_2$, cupric butyrate, $Cu(C_4H_7O_2)_2$, is formed, and, being almost insoluble in water, is at once precipitated, or remains suspended, giving a bluish white opalescent liquid. Cupric valerianate, $Cu(C_5H_9O_2)_2$, is also formed after some time, but is far more soluble than the butyrate, and only slowly collects in the form of greenish oily drops, which gradually pass into greenish-blue hydrous crystalline cupric valerianate (Larocque and Huralt).

QUESTIONS AND EXERCISES

Mention a test for nitrites in potable waters.—Which nitrates are official?—Give the names of some natural and artificial silicates.—"What is soluble glass"?—Distinguish between silica and silicic acid.—How are silicates detected?—What is the quantivalence of silicon?—Mention the sources, formulæ, and analytical reactions of succinates.—State the mode of manufacture of and tests for thiocyanates.—What proportion of tannic acid is contained in galls?—Describe the process for the preparation of tannic acid.—Explain the chemistry of "tanning."—Enumerate the tests for tannic acid.—What is the formula for tannic acid?—Mention official substances other than galls whose astringency is due to tannic acid.—How is gallic acid prepared?—By what reaction is gallic acid distinguished from tannic acid?—Mention the characteristic properties of pyrogallic acid.—Explain the murexid test for uric acid.—Describe the artificial preparation of valerianic acid and other valerianates, giving equations.—What is the formula of valerianic acid?—How are butyrates detected in presence of valerianates?

DETECTION OF THE ACID RADICALS OF SALTS SOLUBLE IN WATER

In examining a salt soluble in water, and concerning which no general information is obtainable, search must first be made for the metallic radical by the appropriate methods (*see* pp. 268, 273, etc.). The metal having been detected, consideration of the character of its salts will indicate which acid radicals may be, and which cannot be, present. Thus, for instance, if the substance under examination is freely soluble in water and lead is found, only the nitric and acetic radicals need be sought, none other of the lead salts than nitrate or acetate being freely soluble in water. Moreover the salt is more likely to be lead acetate than nitrate, for two reasons: the former is more soluble than the latter, and is by far the commoner salt of the two. Medical and pharmaceutical students have probably, in dispensing, already learnt much concerning the solubility of salts, and whether a salt is rarely employed or is in common use. And although but little dependence can be placed on the chances of a salt being present or absent according to its rarity, still the point may have its proper weight. If, in a mixture of salts, ammonium, potassium, and magnesium have been found associated with the sulphuric, nitric, and hydrochloric radicals, and we are asked how we suppose these bodies may have existed in the mixture, we are much more likely to be correct if we suggest that sal-ammoniac, nitre, and Epsom salt were originally mixed together, than if we suppose any other possible combination. Such appeals to experience regarding the solubility or rarity of salts cannot be made by any one unacquainted, or insufficiently acquainted, with the characters of salts; in such cases the relation of a salt to water and acids can be ascertained by referring to the following Table (p. 403) of the solubility or insolubility of about five hundred of the common and rarer salts met with in chemical operations.

The alternative course to the above (namely, to ascertain which acid radicals are present in a mixture, and then to appeal to experience to tell which metallic radicals may be and which cannot be present) is impracticable; for acid radicals cannot be separated out, one after the other, from one and the same quantity of substance by a similarly simple reatment to that already given for metallic radicals. Indeed such a separation of acid radicals could scarcely be accomplished at all, or only by a vast amount of labour. The metallic radicals must therefore be detected first.

Even when the metallic radicals have been found, the acid radicals which may be present must be sought for singly, he chief additional aid which can be brought in being the action of sulphuric acid, a barium salt, a calcium salt, silver nitrate, and ferric chloride on *separate* small portions of the solution under examination, as detailed in the second of the following Tables.

Qualitative Analysis.

Before commencing the analysis of an aqueous solution of a salt or salts, the metallic radicals in which are known, ascertain which acid radicals may be, or, what comes to the same thing, which cannot be present. To this end, consult he following Table (p. 403) of the solubility of salts in water. Look for the name of the metal of the salt in the vertical column; the letters S and I indicate which salts are soluble and which insoluble in water, an asterisk attached to the S neaning that the salt is slightly soluble.

Some of the salts marked as insoluble in water are soluble in aqueous solutions of soluble salts, a few forming soluble double salts. To characterize salts as soluble, slightly soluble, or insoluble, only roughly indicates their relation to water: on the one hand, very few salts are absolutely insoluble in water; on the other, there is a limit to the solubility of every salt.

If only one, two, or perhaps three given acid radicals can be present in the solution, test directly for it or them according to the reactions given in the previous pages. If several may be present, pour small portions of the solution, rendered neutral if necessary by addition of ammonia, into five test-tubes, and add respectively sulphuric acid, barium nitrate or chloride, calcium chloride, silver nitrate, and ferric chloride; then consult the Table on p. 404, in order to interpret correctly the effects these reagents may have produced.

Remarks on the Table, p. 404.

The first point of value to be noticed in connection with this Table, is one of a negative character; namely, if either of the reagents gives no reaction, it is self-evident that the salts which it decomposes with production of a precipitate must be absent. Then, again, if the action of one of the reagents indicates the absence of certain acid radicals, those radicals cannot be amongst those precipitated by the other reagents; thus, if the action of sulphuric acid points to the absence of sulphides, sulphites, carbonates, cyanides, and acetates, these salts may be struck out of the other lists, and the examination of subsequent precipitates is so far simplified. Or, if the barium precipitate is soluble in hydrochloric acid and the calcium precipitate in acetic acid, neither sulphates nor oxalates can be present. Observing these and other points of difference, which will be seen on careful and thoughtful reflection, and remembering the facts suggested by a knowledge of what metallic radicals are present, one acid radical after another may be struck off as absent or present, leaving only one or two as the objects of special experiment. Among the chief difficulties to be encountered

TABLE OF THE SOLUBILITY OR INSOLUBILITY OF SALTS IN WATER.

* The asterisk indicates *slight* solubility.	Acetate.	Arsenate.	Arsenite.	Carbonate.	Chloride.	Citrate.	Chromate.	Cyanide.	Hydroxide.	Iodide.	Nitrate.	Oxalate.	Oxide.	Phosphate.	Sulphate.	Sulphide.	Sulphite.	Tartrate.
Aluminium . .	S	I	I	I	S	S*	I	?	I	?	S	I	I	I	S	I	I	S
Ammonium .	S	S	S	S	S	S	S	S	S	S	S	S	?	S	S	S	S	S
Antimony . .	S	I	I	?	S	?	I	?	I	I	?	S*	I	I	I	I	I	I
Barium . . .	S	I	I	I	S	S*	I	S	S	S	S	I	S	I	I	S	I	I
Bismuth . . .	S	I	?	I	S	S*	I	?	I	I	S	I	I	I	S	I	I	I
Cadmium . .	S	?	?	I	S	S*	?	?	I	S	S	I	I	I	S	I	S	S*
Calcium . . .	S	I	I	I	S	S*	S	S	S*	S	S	I	S*	I	S*	S*	S*	S*
Chromium . .	S	I	?	I	S	S	I	I	I	S	S	S	I	I	S	I	S	S
Cobalt . . .	S	I	I	I	S	S	?	I	I	S	S	I	I	I	S	I	S*	S
Copper . . .	S	I	I	I	S	S	S	I	I	I	S	I	I	I	S	I	I	S*
Ferric . . .	S	I	I	?	S	S	S	?	I	S	S	S*	I	I	S	I	?	S
Ferrous . . .	S	I	I	I	S	S	?	I	I	S	S	S*	I	I	S	I	S*	S*
Gold	?	I	?	?	S	?	?	I	I	I	?	?	I	?	?	I	?	?
Lead	S	I	I	I	S*	S*	I	I	S*	S*	S	I	I	I	I	I	I	I
Magnesium . .	S	I	I	I	S	S	S	?	I	S	S	I	I	I	S	?	S	S
Manganese . .	S	I	?	I	S	I	S	I	I	S	S	I	I	I	S	I	S*	S*
Mercuric . .	S	I	I	I	S	?	S*	S	I	I	S	I	I	I	S	I	?	I
Mercurous . .	S*	I	I	I	I	I	I	?	?	I	S	I	I	I	S*	I	?	I
Nickel . . .	S	I	I	I	S	S	I	I	I	S	S	I	I	I	S	I	S*	S*
Platinum . .	?	I	?	?	S	?	?	?	I	S*	S	?	I	?	S	I	S	?
Potassium . .	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Silver . . .	S*	I	I	I	I	I	I	I	?	I	S	I	I	I	S*	I	I	I
Sodium . . .	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Stannic . . .	S	?	I	?	S	?	I	?	I	S	S	S	I	I	S	I	?	?
Stannous . .	S	I	I	?	S	?	I	?	I	S	S	I	I	I	S	I	I	S
Strontium . .	S	I	I	I	S	I	I	S	S	S	S	I	S	I	I	S	I	S*
Zinc	S	I	?	I	S	S*	S*	I	I	S	S	I	I	I	S	I	S*	S*

TABLE TO AID IN THE DETECTION OF CHLORIDES, BROMIDES, IODIDES, CYANIDES, NITRATES, CHLORATES, BORATES, ACETATES, SULPHIDES, SULPHITES, SULPHATES, CARBONATES, OXALATES, TARTRATES, PHOSPHATES, AND CITRATES IN A NEUTRAL AQUEOUS SOLUTION.

(For remarks concerning this Table, *see* pp. 402 and 405.)

SULPHURIC ACID DECOMPOSES	BARIUM CHLORIDE PRECIPITATES	CALCIUM CHLORIDE PRECIPITATES	SILVER NITRATE PRECIPITATES	FERRIC CHLORIDE PRECIPITATES	NOT PRECIPITATED.
Sulphides, Sulphites, and Carbonates, with effervescence—hydrogen sulphide and sulphurous anhydride, known by their odour, and carbonic anhydride, which has no special odour, being evolved. Cyanides, with production of the odour of hydrocyanic acid. Acetates, with production of the odour of acetic acid when the solution is warmed. (For other salts, *see* p. 405).	Borates. Sulphites. Sulphates. Carbonates. Oxalates. Tartrates. Phosphates. Citrates. Of these white barium precipitates, the sulphate is the only one insoluble in hydrochloric acid; the tartrate and citrate char when heated on platinum foil; the sulphite and carbonate are decomposed by acids with effervescence.	Borates. Oxalates. Sulphites. Tartrates. Sulphates. Phosphates. Carbonates. Citrates. Of these white calcium precipitates, the sulphate only is sol. in much water; the borate, carbonate, and citrate are sol., when fresh, in solution of ammonium chloride: all are sol. in acetic acid except oxalate and some tartrate and sulphate; all are sol. in hydrochloric acid, much sulphate excepted; the dry tartrate and citrate char when heated: the sulphite and carbonate effervesce with acids.	Chlorides, white. Bromides, white. Iodides, yellow. Cyanides, white. Borates, white. Sulphides, black. Sulphites, white. Carbonates, white. Oxalates, white. Tartrates, white. Phosphates, yellow. Citrates, white. Of these silver precipitates, the chloride, bromide, iodide, cyanide, and sulphide are insoluble in dilute nitric acid; the others soluble. Silver oxalate is sparingly soluble.	Borates, yellowish. Sulphides, black. Carbonates, reddish. Oxalates, yellow. Phosphates, yellow-white. Gives red colour with acetates, if neutral. (For other salts, *see* p. 405.)	Nitrates. Chlorates. Acetates. Apply special tests.

Note.—The student should practise the examination of aqueous solutions of salts until able to detect acid radicals with facility and precision. For this purpose he may finish the analyses of salts or solutions already examined for metallic radicals, or have aqueous solutions of salts, or the salts themselves, specially prepared for present use by a friend, the metals of the salts being stated. He will then be in a position to study effectively the analysis of salts which may or may not be soluble in water, examining them for both metallic and acid radicals (*see* p. 406).

will be the separation from each other of chlorides, bromides, iodides, and cyanides, or of tartrates from citrates, and confirmatory tests of the presence of certain compounds. These may all be surmounted on referring back to the reactions of the various radicals as described under their hydrogen salts, the acids.

In rendering a solution neutral, for the application of the various group-tests, the necessary employment of any large amount of acid or of alkali must be noted, the presence of alkaline hydroxides or of free acids, respectively, being thereby indicated. The presence of free acid is usually indicated by the *abundant* effervescence which results on the addition of a carbonate.

Sulphuric acid, the first group-reagent, may itself yield by reduction, especially when heated with certain solid substances, sulphurous acid or hydrogen sulphide (*see* pp. 327 and 293); hence the production of these from a *diluted* solution should alone be regarded as evidence of the presence of a sulphide or sulphite.

Calcium chloride does not precipitate citrates readily or completely in the cold: therefore the mixture should be filtered and the filtrate boiled; calcium citrate then separates. Calcium tartrate is soluble in solution of ammonium chloride when quite freshly precipitated, but not after it has become crystalline. From their solutions in ammonium chloride, calcium tartrate is mostly precipitated by ammonia, and calcium citrate on boiling.

The rarer acid radicals will be very seldom met with. The presence of *benzoates, hippurates* (which give benzoic acid), *hypochlorites, thiosulphates, nitrites,* and *valerianates* will be indicated during the treatment with sulphuric acid. *Ferrocyanides, ferricyanides, meconates, succinates, thiocyanates, tannates,* and *gallates* are among the salts whose presence is indicated by ferric chloride; *formates, hypophosphites, malates,* and others are indicated by silver nitrate. *Urates* char when heated, giving an odour resembling that of burnt feathers.

In actual practice the analyst nearly always has some clue to the nature of rarer substances placed in his hands.

If chromium and arsenium have been detected among the metallic radicals, these elements may be present in the form of *chromates, arsenates,* and *arsenites,* yielding with barium chloride yellow barium chromate and white barium arsenate and arsenite, and with silver nitrate red silver chromate, brown silver arsenate, and yellow silver arsenite.

QUESTIONS AND EXERCISES

In analysing an aqueous solution of salts, for which radicals would you first search, the metallic or the acid, and why?—In an aqueous solution there have been found magnesium (Mg) and potassium (K), with the sulphuric radical (SO_4), and iodine (I); state which salts were probably dissolved originally in the water, and mention the considerations which guide you to the conclusions.—Give a sketch of the methods by which you would examine a neutral or only faintly acid aqueous liquid for the acid radicals which might be present. In what stages of the examination would the following salts be detected? *a.* Carbonates and Sulphates. *b.* Oxalates. *c.* Tartrates and Nitrates. *d.* Acetates and Sulphites. *e.* Bromides and Cyanides. *f.* Borates. *g.* Iodides and Phosphates. *h.* Chlorates, Oxalates, and Acetates. *i.* Chlorides and Iodides. *j.* Sulphites. *k.* Sulphides, Carbonates, and Nitrates. *l.* Citrates and Sulphates.—Silver nitrate gives no precipitate in a given aqueous solution; what acid radicals may be present?—Barium chloride gives no precipitate in a given neutral solution, but silver nitrate gives a white precipitate; what acid radicals are indicated?—Ferric chloride produces a deep-red colour in a solution, calcium chloride yielding no precipitate; what salts may be present, and how may they be distinguished from each other?—Ferric chloride gives a black precipitate in a solution in which sulphuric acid develops no odour; to what is the effect due?

ANALYSIS OF SALTS

SINGLE OR MIXED, SOLUBLE OR INSOLUBLE

Thus far, most of the substances which have been considered, especially those of pharmaceutical interest, have been regarded as definite compounds, and as having certain well-defined radicals termed metallic and acid respectively: moreover attention has been designedly restricted to those definite compounds which are soluble in water. But there still are numerous substances having no definite or known composition; and of those having definite composition there are many having no definitely ascertained radicals. Again, of those having definite composition, and whose constitution has been in part or entirely elucidated, there are many insoluble in water.

Chemical substances of whose composition or constitution little or nothing is at present known, are chiefly of animal and vegetable origin ; they are not of immediate importance, and may be omitted from consideration here.

Of substances which are definite in composition, but whose parts or radicals are unknown or imperfectly known, there are only a few (such as the alkaloids, amylaceous and saccharine matters, the glucosides, and the albumenoid, resinoid, and animal and vegetable colouring matters) which have any considerable amount of medical or pharmaceutical interest ; these will be noticed subsequently.

Definite compounds most frequently present themselves ; and of these by far the larger proportion (namely, the salts soluble in water) have already been studied. There remain, however, many salts which are insoluble in water, but which must be brought into a state of solution before they can be effectively examined. The next subject of laboratory work is, therefore, the analysis of substances which may or may not be soluble in water. This will involve no other analytical schemes than those which have been given, and will in only one or two cases increase the difficulty of the analysis of a precipitate produced by a group-reagent ; but it will give roundness, completeness, and a practical bearing to the student's analytical knowledge. Such laboratory work will at the same time bring into notice the methods by which substances insoluble in water are manipulated for pharmaceutical purposes, or are made available for use as food for plants, or as food or medicine for man and animals generally.

Preliminary Examination of Solid (chiefly mineral) Salts.

Before attempting to dissolve a salt for analysis, its appearance and other physical properties should be noted, and the influence of heat and concentrated sulphuric acid should be ascertained. Unless the operator knows how to interpret what is thus observed, and to what extent he can place confidence in his observations, he should omit the preliminary examination altogether, except when he is able to follow it out under the guidance of a judicious teacher ; for it is impracticable here to do more than hint at the results which may be obtained by such an examination, or so to adapt descriptions as to prevent a student allowing unnecessary weight to attach to preconceived ideas.

Whatever be the course pursued, short memoranda describing results should invariably be entered in the note-book.

1. Examine the physical characters of the salt in various ways, but only rarely and cautiously, by the palate, on account of the danger of so doing.

If the salt is, to the eye, white, little more than traces of distinctly coloured substances can be present; if coloured, the tint may indicate the nature of the substance or of one of its constituents, supposing that the student is already acquainted with the colours characteristic of certain salts. Closer observation, aided perhaps by a lens, may reveal the presence, in a pulverulent mixture, of small crystals or pieces of a single substance; these should be picked out by means of a needle or forceps and examined separately. In a powder or roughly pulverized mixture of substances, the process of *sifting* (through such sieves as muslin of different degrees of fineness) often mechanically separates substances, and thus greatly facilitates analysis. The substance may present an undoubted metallic appearance, in which case only the metals existing under ordinary atmospheric conditions need, as a rule, be sought for. Peculiarity in smell reveals the presence of ammonia, hydrocyanic acid, hydrogen sulphide, etc. Between the fingers a substance is, perhaps, hard, soft, or gritty, and from such a character useful inferences may be drawn. Or the substance may be heavy, like the salts of barium or lead, or light, like the magnesium carbonates and oxides; or it may be one of the pharmaceutically well-known class of "scale" preparations.

2. Place a grain or two of the salt in a dry test-tube or in a piece of glass tubing closed at one end, and heat it, at first gently, then more strongly, and finally, if necessary, in the blowpipe-flame.

Gases or vapours of characteristic appearance or odour may be evolved, such as iodine, nitrous fumes, sulphurous anhydride, hydrocyanic acid, or ammonia. Much steam given off by a dry substance indicates either hydroxides or salts containing water of crystallization. (A small quantity of interstitial moisture often causes heated crystalline substances to *decrepitate*—from *decrepo*, I crackle—that is, break up with slight explosive violence, owing to the expansive force of the steam suddenly generated.) A sublimate may result, due to salts of ammonium, mercury, or arsenium, to oxalic or benzoic acid, or to sulphur free or as a sulphide—a salt wholly volatile containing such substances only. The compound may blacken, pointing to the presence of organic matter—which, in ordinary salts, will probably be in the form of acetates, tartrates, and citrates, or as common salts of the alkaloids morphine, quinine, strychnine, or as starch, sugar, salicin; or it may be in other definite or indefinite forms common in pharmacy, and for which tests will be given in subsequent pages. If no charring occurs, the important fact is established that organic matter is not likely to be present—except perhaps cyanides, formates, or oxalates, which do not char. The residue may change colour from the presence or development of zinc oxide, iron oxide, etc., or melt from the presence of a fusible salt and absence of any large proportion of infusible salt, or be unaltered, showing the absence of any large amount of such substances.

3. Place a grain or two of the salt in a test-tube, add a drop or two of concentrated sulphuric acid, *cautiously* smelling any gas that may be evolved; afterwards slowly heat the mixture, noticing the effect, and stopping the experiment when any sulphuric fumes begin to escape.

Iodine, bromine, and nitrous or chlorine-like fumes will reveal themselves by their colour, indicating the presence of iodides, iodates, bromides, bromates, nitrates, and chlorates. The evolution of a colourless gas, fuming on coming into contact with air and having an irritating odour, points to chlorides, fluorides, or nitrates. Gaseous products having a greenish colour and odour of chlorine indicate chlorates, hypochlorites, or chlorides mixed with other substances. Slight sharp explosions betoken chlorates. Evolution of colourless gas may proceed from cyanides, acetates, sulphides, sulphites, carbonates, or oxalates. Charring will be due to citrates, tartrates, or other organic matter. If none of these effects is produced, most of the above-named substances are absent or only present in minute proportion. The substances apparently unaffected by the treatment are metallic oxides, borates, sulphates, and phosphates.

4. Expose some of the substance to the blowpipe-flame on platinum wire, with or without a bead of borax or of microcosmic salt * (sodium, ammonium, hydrogen phosphate, $NaNH_4HPO_4,4H_2O$); on platinum foil, or in a porcelain crucible, or on a crucible lid, with or without sodium carbonate; or on charcoal, alone or in conjunction with sodium carbonate, potassium cyanide, or cobalt nitrate. This experiment will sometimes yield important information, especially to one who has devoted much attention to reactions producible by the blowpipe-flame. The medical or pharmaceutical student, however, will seldom have time to work out this subject to an extent sufficient to make it a trustworthy guide in analysis.

Methods of Dissolving and Analysing Single or Mixed Solid Substances.

Having submitted the substance to preliminary examination, proceed to dissolve and analyse by the following methods. These operations consist in treating the well-powdered substance consecutively with cold or hot water, hydrochloric acid, nitric acid, nitro-hydrochloric acid, or fusing with alkali-metal carbonates and dissolving the product in water and acid. The resulting liquids are analysed in the manner already described, or by slightly modified processes as detailed in the following paragraphs.

Solution in Water.—Boil about a grain of the salt presented for analysis in about a third of a test-tubeful of water. If it dissolves, prepare a solution of about 20 or 30 grains in half an ounce or more of water, and *proceed with the analysis in the usual way*, testing first for the metallic radical or radicals by the proper group-reagents (HCl, H_2S, NH_4SH, $(NH_4)_2CO_3$, $(NH_4)_2HPO_4$), p. 273, and then for the acid radical or radicals, directly or by aid of the prescribed reagents (H_2SO_4, $BaCl_2$, $CaCl_2$, $AgNO_3$, $FeCl_3$), p. 404.

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* So called because formerly obtained from the urine of man, who was called the *microcosmos*, or *little world*.

If the salt is not *wholly* dissolved by the water, ascertain whether or not any has entered into solution, by filtering, if necessary, and cautiously evaporating a drop or two of the clear liquid to dryness on platinum foil; the presence or absence of a residue gives the information sought for. If anything is dissolved, prepare a sufficient quantity of solution for analysis and proceed as usual, reserving the insoluble portion of the mixture, after thoroughly exhausting with water, for subsequent treatment with acids.

Solution in Hydrochloric Acid.—If the salt is insoluble in water, digest about a grain of it (or of the insoluble portion of a mixed salt) in a few drops of hydrochloric acid, adding water and boiling if necessary. If the salt wholly dissolves, prepare a sufficient quantity of the liquid, noticing whether or not any effervescence (due to the presence of sulphides, sulphites, carbonates, or cyanides) occurs, and proceed with the analysis as before, except that the first step, the addition of hydrochloric acid, may be omitted.

The analysis of this solution will in most respects be simpler than that of an aqueous solution inasmuch as the majority of salts (all those soluble in water) will be absent. This acid solution will, in short, only contain:—chlorides produced by the action of the hydrochloric acid on sulphides, sulphites, carbonates, cyanides, oxides, and hydroxides; and certain borates, oxalates, phosphates, sulphates, tartrates, and citrates (possibly silicates and fluorides), which are insoluble in water, but soluble in acids without apparent decomposition. Sulphides, sulphites, carbonates, and cyanides will have revealed themselves by the occurrence of effervescence during solution; and the presence of oxides and hydroxides may (p. 115) be inferred by the absence of compatible acid radicals. The borates, oxalates, phosphates, tartrates, and citrates alluded to will be reprecipitated in the systematic analysis as soon as the acid of the solution is neutralized; that is, will come down as such when ammonia and ammonium hydrosulphide are added in the usual course. Of these precipitates, only the calcium oxalate and the calcium and magnesium phosphates need occupy attention now, for barium oxalate and phosphate seldom or never occur, and the borates, tartrates, and citrates met with in medicine or general analysis, are all soluble in water. These phosphates and oxalates, then, will be precipitated in the course of analysis along with iron, their presence not interfering with the detection of any other metal. If, from the unusually light colour of the ferric precipitate, phosphates and oxalates are suspected, it is treated according to the following Table :—

PRECIPITATE OF PHOSPHATES, OXALATES, FERRIC HYDROXIDE, ETC.

Dissolve in HCl, add citric acid, then NH_4OH, and filter; then follow the Table below.

<table>
<tr>
<td rowspan="3">Filtrate
Fe
Add HCl and
$K_4FeC_6N_6$
Blue ppt.</td>
<td colspan="3">Precipitate
$Ca_3(PO_4)_2$, CaC_2O_4, $Mg_3(PO_4)_2$
Boil in acetic acid, and filter.</td>
</tr>
<tr>
<td rowspan="2">Insoluble
CaC_2O_4*
White
(CaF_2 *may* occur here.)</td>
<td colspan="2">Filtrate
$Ca_3(PO_4)_2$, $Mg_3(PO_4)_2$
Add $(NH_4)_2C_2O_4$, stir, filter.</td>
</tr>
<tr>
<td>Precipitate
white
indicating
$Ca_3(PO_4)_2$</td>
<td>Filtrate
add NH_4OH.
White ppt.
$MgNH_4PO_4$</td>
</tr>
</table>

In analysing phosphates and oxalates, advantage is also frequently taken of the facts that the phosphoric radical is wholly removed from solution of phosphates in acid by the addition of an alkali-metal acetate and ferric chloride, and subsequent ebullition, as described under "Phosphoric Acid" (p. 361), and that dry oxalates are converted into carbonates by ignition as mentioned under "Oxalic Acid" (p. 345).

Certain arsenates and arsenites, insoluble in water but soluble in hydrochloric acid, may accompany the above phosphates and oxalates if from any cause hydrogen sulphide has not previously been passed through the solution, or has only been passed for an insufficient length of time.

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* Most oxalates, after ignition, effervesce on the addition of acid; fluorides may be detected by the "etching" test.

If the substance insoluble in water does not *wholly* dissolve in hydrochloric acid, ascertain if any has entered into solution, by filtering, if necessary, and evaporating a drop of the clear liquid to dryness on platinum foil; the presence or absence of a residue gives the information sought for. If anything is dissolved, prepare a sufficient quantity of solution for analysis, and proceed as usual, reserving the insoluble portion of the mixture, after thoroughly exhausting with hydrochloric acid and well washing with water, for the following treatment by nitric acid.

Solution in Nitric Acid.—If the salt is insoluble in water and hydrochloric acid, boil it (or that part of it which is insoluble in these menstrua) in a few drops of nitric acid. If it wholly dissolves, remove excess of acid by evaporation, dilute with water, and proceed with the analysis.

This nitric acid solution can contain only a few substances; for nearly all salts soluble in nitric acid are also soluble in hydrochloric acid, and therefore will have been removed previously. Some of the metals, however (Ag, Cu, Hg, Pb, Bi), as well as amalgams and alloys, unaffected or scarcely affected by hydrochloric acid, are readily attacked and dissolved by nitric acid. Many of the sulphides, also, insoluble in hydrochloric acid, are dissolved by nitric acid, usually with separation of sulphur. Calomel is converted, by long boiling with nitric acid, into mercuric chloride and nitrate. The nitrates here produced are soluble in water.

The nitric acid solution, as well as the hydrochloric acid and aqueous solutions, should be examined separately. Apparently, time would be saved by mixing the three solutions together and making one analysis. But the object of the analyst is to separate every radical from every other; and when this has been partially accomplished by solvents, it would be unwise to again mix and separate a second time. Moreover, solvents often do what the chemical reagents cannot do—namely, separate *salts* from each other. This is important, inasmuch as the end to be attained as far as possible in analysis is not only an enumeration of the radicals present, but a knowledge of the actual condition in which they are present; the analyst must state, when this is possible, of what salts a given mixture was originally formed—how the metallic and acid radicals were originally distributed. In attempting this, much must be left to theoretical considerations, and it is often impossible to arrive at certainly accurate conclusions; but a process by which the salts themselves are separated is of practical assistance, hence the chief advantage of analysing separately the solutions resulting from the action of water and acids on a solid substance.

Solution in Nitro-Hydrochloric Acid.—If the salt or any part of a mixture of salts is insoluble in water, hydrochloric acid, and nitric acid, digest it in nitro-hydrochloric acid, warming, or even boiling gently, if necessary; evaporate to remove excess of acid, dilute, and proceed as before.

Mercuric sulphide and substances only slowly attacked by hydrochloric or nitric acid, as, for example, calomel and ignited ferric oxide, are sufficiently altered by the free chlorine of aqua regia to become soluble.

Analysis of Insoluble Substances.

If the substance is insoluble in water and acids, it is one or more of the following substances:—Sand and certain silicates, such as pipeclay and other clays; fluor spar; cryolite, Na_3AlF_6; barium, strontium, and possibly calcium sulphates; tinstone; antimonic oxide; glass; felspar (aluminium and alkali-metal silicates); silver chloride, bromide, or iodide; lead sulphate. It may also be or contain carbon or carbonaceous matter, in which case it is black and combustible, burning entirely or partially away when heated in the air —or it may be or contain sulphur, in which case sulphurous anhydride is evolved, detected by its odour, when the substance is heated in air. A drop of solution of ammonium hydrosulphide added to a little of the powder will at once indicate the presence or absence of salts of such metals as lead and silver. For the other substances, proceed according to the following (Bloxam's) method:—

Four or five grains of the dry substance are intimately mixed with twice the quantity of dried sodium carbonate, and this mixture is well rubbed in a mortar with five times its weight of *deflagrating flux* (1 of finely powdered charcoal to 6 of nitre). The resulting powder is placed in a thin porcelain dish, or crucible, or clean iron tray, and a lighted match applied to the centre of the heap. Deflagration ensues, and decomposition of the various substances occurs, the acid radicals going to the alkali-metals to form salts soluble in water, the metallic radicals being simultaneously converted into carbonates or oxides. The mass is boiled in water for a few minutes, the mixture filtered, and the residue well washed. The filtrate may then be examined for acid radicals and aluminium, tin, etc., and the residue be dissolved in dilute hydrochloric acid and analysed by the ordinary method.

The only substance which resists this treatment is chrome iron-ore.

To detect alkali in felspar, glass, or cryolite, Bloxam recommends deflagration of the powdered mineral with one part of sulphur and six of barium nitrate. The mass is boiled in water, the mixture filtered, ammonium hydroxide and carbonate added to remove barium, the mixture again filtered, and the filtrate evaporated and examined for alkali-metals by the usual process.

Hydroxides and Oxides.

If no acid radical can be detected in a substance, or if the quantity found is obviously insufficient to saturate the quantity of metallic radical present, the occurrence of oxides or hydroxides, or both, may be suspected. Confirmation of their presence will be found in the general rather than in any special behaviour of the substances. Some hydroxides yield water when heated—in a dry test-tube held nearly horizontally in the flame, so that moisture may condense on the cool part of the tube. Some oxides yield oxygen—detected by heating in a test-tube, and inserting the incandescent end of a strip of wood. Soluble hydroxides cause abundant evolution of ammonia when heated with solution of ammonium chloride.* Soluble hydroxides also give characteristic precipitates with the various metallic solutions. Hydroxides and oxides insoluble in water, not only neutralize much nitric acid, or acetic acid, but are thereby converted into salts soluble in water. Most oxides and hydroxides have a characteristic appearance. In short, some one or more properties of an oxide or a hydroxide will generally betray its presence to the student who not only has knowledge respecting chemical substances, but has cultivated the faculties of observation and perception.

Fractional Operations.

Not only is the common process of *sifting* (p. 408) through sieves of varying degrees of fineness a useful fractional operation or separatory adjunct in analytical as in other work, but also fractional *elutriation* (p. 144), fractional *solution* of a mixed mass by *lixiviation* (p. 89) of the substance with successive small quantities of solvents, and fractional *precipitation* with filtration after each addition of successive small quantities of a precipitant are often valuable aids. Fractional *distillation* (*see* p. 485) is often very useful, fractional *sublimation* (p. 98) and fractional *crystallization* (p. 81) occasionally, fractional *fusion* less often.

QUESTIONS AND EXERCISES

Describe the preliminary treatment to which a salt may be subjected prior to systematic analysis.—Mention substances which might be recognised by smell.—Mention some salts which are heavy, and some which are light.—Name some substances recognisable by their colour.—What inference may be drawn from the appearance of steam when dry substances are heated?—Why do certain crystals decrepitate?—If a powder sublimes on being heated, to what classes of compounds may it belong?—When heat causes charring, what conclusion is drawn?—No change occurring by heat, what substances cannot be present?—Give examples of salts which are identified by their behaviour with concentrated sulphuric acid, and by their comportment in the blow-pipe flame, with or without borax or microcosmic salt.—What are the solvents usually employed in endeavouring to obtain a substance in a state of solution, and what is the order of their application?—Name a few salts which may be present in an aqueous solution.—Mention some common compounds insoluble in water, but soluble in hydrochloric acid.—What substances are only attacked by nitric acid or nitro-hydrochloric acid?—At what stage of analysis do arsenites and arsenates show themselves?—Sketch a method for the complete analysis of a liquid suspected to be an aqueous solution of neutral salts.—How can earthy phosphates and oxalates and ferric hydroxide be separated from each other?—How would you proceed to analyse an alloy?—By what process may substances insoluble in water or acids be analysed?—How would you qualitatively analyse glass?

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* Red litmus-paper placed over the mouth of a test-tube in which ammonium chloride solution alone is being boiled turns blue, but phenol-phthalein paper is not affected.

THEORY OF SOLUTION

The phenomena of electrolysis have given rise to a new theory of solution. Formerly a salt was supposed to consist of a basic oxide combined with an acid oxide; thus "sulphate of soda" (as the salt now known as sodium sulphate was called) was regarded as Na_2O,SO_3. When a solution of sodium sulphate is electrolysed (*see* p. 63), caustic soda is formed at the negative, and sulphuric acid at the positive electrode; these substances were supposed to be produced by the union of the sodium oxide with water at the negative electrode and of the sulphuric anhydride with water at the positive electrode. To account for such phenomena a new theory has, however, been brought forward, according to which, a salt—*e.g.*, sodium sulphate—when dissolved in water splits up into an electro-positive and an electro-negative part, but these are now supposed to be, not the basic oxide and the acid oxide, but the metallic or basic radical and the acid radical. Sodium atoms or *ions* constitute the positive part, sulphate radicals or sulphations (SO_4) the negative part; when an electrical current is passed through the solution the former lose their charges of positive electricity at the negative electrode and then act on the water, forming caustic soda and liberating hydrogen; the sulphations similarly lose their charges of negative electricity and then decompose the water at the positive electrode, forming sulphuric acid and liberating oxygen. When Arrhenius brought forward this view, a new theory of solution was much needed, for it had been found by careful measurements that the thermal change involved in the act of solution could not be entirely accounted for by the physical change of state. Arrhenius assumed that a salt on passing into solution undergoes more or less complete separation into its ions (ionization), and that its ions act independently of each other, not only in electrolytic, but also in chemical processes. In general, we find chemical activity, in the sense of readiness to undergo double decomposition, to go hand in hand with electrical conductivity, and his explanation is that the real carriers of the electricity are the free ions, which, by virtue of their freedom, are chemically active, since they have not to be separated from each other before they interact.

This hypothesis of the existence of free ions in solution has thrown much light on the general behaviour of salt solutions, and has rendered possible an explanation of many hitherto inexplicable phenomena.

THE PERIODIC LAW

When the elements are arranged in the order of their atomic weights, it is found that, starting with lithium, the chemical properties of each successive element differ in many cases only to a relatively small degree from those of the element immediately preceding. This holds for a "period" of (at first) seven elements, and then the eighth element shows a sharp change of properties from those of the seventh and a striking resemblance to those of the first; the ninth resembles the second, the tenth resembles the third, and so on. The first two periods consist of seven elements each; the subsequent ones, which are more or less complete, of seventeen each. In the following Table the periods are arranged in perpendicular columns, whereby kindred elements are to a large extent brought side by side in the same horizontal lines :—

Table of the Elements, arranged to illustrate the Periodic Law.

	...		...	K	38·83	Rb	84·8	Cs	132		...		...
	...		...	Ca	39·71	Sr	86·94	Ba	136·40		...		...
	...		...	Sc	43·8	Y	88·3	La	137·9	Yb	171·7		...
	...		...	Ti	47·7	Zr	89·9	Ce	139·20		...	Th	230·8
	...		...	V	50·8	Cb	93·3		...	Ta	181·6		...
	...		...	Cr	51·74	Mo	95·3		...	W	182·6	U	236·7
	...		...	Mn	54·52		...		...		...		...
	...		...	Fe	55·60	Ru	100·9		...	Os	189·6		...
	...		...	Ni	58·3	Rh	102·2		...	Ir	191·5		...
	...		...	Co	58·56	Pd	105·7		...	Pt	193·30		...
Li	6·97	Na	22·88	Cu	63·12	Ag	107·11		...	Au	195·70		...
Gl	9·03	Mg	24·18	Zn	64·91	Cd	111·6		...	Hg	198·80		..
B	10·85	Al	26·90	Ga	69·5	In	113·1		...	Tl	202·6		...
C	11·91	Si	28·2	Ge	71·9	Sn	118·20		...	Pb	205·35		...
N	13·94	P	30·80	As	74·50	Sb	119·00		...	Bi	207·30		...
O	15·88	S	31·82	Se	78·6	I	125·9		...		...		...
F	18·9	Cl	35·19	Br	79·35	Te	126·6		...		...		...

It will be noticed that there are gaps in the Table suggesting elements yet to be discovered, or indicating uncertainty as to the correct position of a number of known elements; also that there are irregularities suggesting the desirability of reconsidering some of the present atomic weights. Other difficulties also occur, but still the regularities are so striking as to show clearly that the properties of the elements are in some way dependent on their atomic weights.

The nature of some of the progressive relations to each other of the members of the first two periods are illustrated by the formulæ of certain of their compounds when placed side by side, as under. Where blanks occur, either no compound at all, or no illustrative compound, is known.

Compounds with oxygen :—

Li_2O	GlO	B_2O_3	CO_2	N_2O_5	—	—
Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_2	—

Compounds with hydrogen:—

—	—	—	CH_4	NH_3	OH_2	FH
—	—	—	SiH_4	PH_3	SH_2	ClH

Compounds with chlorine:—

$LiCl$	$GlCl_2$	BCl_3	CCl_4	NCl_3	OCl_2	—
$NaCl$	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	SCl_2	—

The compounds formulated above are not the whole of the oxygen, hydrogen, and chlorine compounds of the various elements, but are chosen to illustrate regularities as far as possible. There are, however, a number of irregularities in these periods, and in the subsequent periods irregularities become more numerous.

Since the position of an element in the above Table is fixed by its atomic weight, and since it has been found that the properties of an element and the character of its compounds can be foreseen to a certain extent from those of its neighbours in the Table, above and below, right and left, the general statement has been enunciated, based upon this periodic arrangement and supported by a great deal of evidence, that *the properties of an element and the nature of its compounds are functions of its atomic weight.*

An inspection of the foregoing Table shows how groups of allied elements are brought close together. Thus the halogens (with the exception of iodine*) all fall into one line, and the same is true of the groups of kindred elements, calcium, strontium, and barium; nitrogen, phosphorus, arsenium, and antimony; etc. Further, each of the first five periods is headed by an alkali metal. The symbols printed in black type are those for the small group of elements usually classed as non-metals, and indicate the remarkable nature of the position of these elements in the periodic system of classification.

Advice to Students respecting the Method of Studying the following pages on Organic Chemistry.

Both medical and pharmaceutical students of organic chemistry may be divided into two classes, namely: *junior*

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* It seems as if the true position of iodine in the periodic system should be after instead of before tellurium. The respective places assigned to iodine and tellurium depend, however, upon the determinations of the atomic weights of these elements which are considered to be the most reliable.

students, or those who, in the first instance at all events, desire to obtain only a general acquaintance with the subject, and *senior students,* or those who, having some general information, desire further knowledge of this branch of the science. To the members of each of these classes who use this Manual, some advice concerning the kind and extent of work they may hope to accomplish in this department of the science will perhaps be acceptable.

Junior Students.—The whole of the following section on organic chemistry should be read through carefully once or twice, with the object, not so much of remembering all that is stated, as of acquiring (*a*) a general view of the scope of the subject, (*b*) a clear notion of the modes of classifying organic substances, and (*c*) an intelligent perception of their broad relationships to one another. Special attention should be given to the methods of preparing and testing the particular substances officially recognised in the British Pharmacopœia, the student of practical chemistry preparing actual specimens of most of these substances, as well as studying their analytical reactions and testing for impurities in them. He should prepare small quantities of chloroform, iodoform, spirit of nitrous ether, acetic ether, and a volatile oil; should extract gum from a gum-resin, purify some benzene, test aloin, and examine methylated spirit for methyl alcohol; prepare some alcohol by fermentation, concentrating the product until it will burn; make ether; convert amyl alcohol into valerianic acid; test carbolic acid and glycerin; manufacture a specimen of soap; extract mannite from manna; examine the analytical reactions of cane and grape sugars; obtain starch from wheat-flour, maize-flour, and a potato, and examine each product with the microscope; make dextrin, pyroxylin, and collodion; prepare and test aldehyde, and try the action of lime on chloral hydrate; prepare and test acetic, oxalic, and citric acids; emulsify sweet and bitter almonds: prepare elaterin, and test jalap-resin and salicin; extract morphine or quinine, or both, and perform the tests for the chief alkaloids of opium, cinchona, and nux vomica; test albumen and pepsin. Having gone through these operations, he should read again through the whole section.

Senior Students, having done all that junior students are, in the previous paragraph, advised to do, should thoughtfully study every page, reading what one other author, at least, has to say on each subject. More especially they should actually prepare, or test, or otherwise *experiment* with, one or more typical members of most of the series, or sub-series, of organic substances. For example, they should prepare the *hydrocarbon* methane (from sodium acetate), convert it into a *haloid derivative* (by one of the given methods), transform this into the *alcohol* (by the agency of silver oxide and water), and this again into the *acid* (by oxidation). The preparation of acetylene, and ethylene, and some of their derivatives, should be tried; the differences between turpentine and petroleum spirit should be experimentally proved; nitro-benzene should be made, this be converted into aniline, and this again into "mauve"; aloin should be prepared; methyl alcohol be extracted from crude wood spirit, and absolute alcohol be obtained from "alcohol (90 per cent.)"; alcohol and acetic acid should be regenerated from the acetic ether previously prepared (by ebullition with a concentrated aqueous solution of caustic potash); ethyl iodide or bromide and perhaps zinc-ethyl be made; glycol be prepared and then oxidized; glycerin be examined; starch be converted into dextrin and into sugar; malt extract be examined for diastase; trinitrocellulin be made; acetaldehyde be fully examined and aldehyde-ammonia prepared; lactic acid be made; benzoic and salicylic acids and aldehydes be obtained; natural urea be extracted and artificial urea made; the glucosides be examined; and one or two artificial alkaloids be prepared; etc. Melting-points and boiling-points of pure substances should be taken; and fractional distillation should be applied either to acetic acid with a view to separate glacial acid on the one hand from water or weak aqueous acid on the other, to mixed alcohol and water with the object of attempting their re-separation as far as possible, or to some such mixture. Especially must the operations of quantitative analysis of organic compounds, in due time, be fully and thoroughly performed.

Other Students.—Students who have no occasion to apportion their periods of study in the manner contemplated in the previous paragraphs are recommended to go through the succeeding sections as they have gone through the foregoing, namely, page by page.

ORGANIC CHEMISTRY *

Introduction

With the exception of alcohol, some acids and their salts, and a few other substances, the large number of compounds which have hitherto engaged the student's notice in this Manual have been of mineral origin. But the two other kingdoms of Nature, the animal and vegetable, furnish still larger numbers of definite compounds. We shall now proceed to the consideration of these—the latter chiefly.

In its original signification what was termed Organic Chemistry (*ὄργανον*, *organon*, an organ) embraced the chemistry of those substances which were known only as products of the vital processes which take place within the tissues of plants and of animals; and, further, the chemistry of the various products derived from these substances, or from the tissues themselves, by subsequent treatment in the laboratory. The separate classification and consideration of these substances formerly seemed expedient in view of the fact that none of them could then be obtained by the ordinary operations of the chemical laboratory, starting from non-organized materials. The term "organic" as originally applied to any substance was thus intimately associated with the view that organized matter—living matter, or matter which had at one time formed part of a living plant or animal—was necessary for its production. Methods are now known, however, whereby a considerable number of substances which are identical in every respect with known products of animal or of plant life

* Students will find that in taking up the subject of organic chemistry they are not departing from the method of study hitherto pursued. Hitherto they have concentrated attention on the chief elements, one at a time; they are now about to investigate the compounds of one of those elements which possesses a greater range of combining powers than any other that has been examined. Organic chemistry is the chemistry of the element *carbon*.

(or with derivatives from these) can be prepared in the laboratory "artificially," as it is often termed, from purely inorganic materials.

Organic chemistry has been defined in more recent times as the chemistry of the compounds of carbon. There does not, however, now seem to be any good reason for classing as organic, the oxygen compounds and some other relatively simple compounds of carbon, including many of the naturally occurring mineral carbonates; more particularly as these must, for the sake of completeness, be dealt with under the heading of inorganic chemistry. It is thus impossible to fix the bounds of inorganic and of organic chemistry respectively, unless an arbitrary line is drawn, which shall mark a distinction that is wholly artificial, and is not founded upon any real difference in the general nature of the facts and principles treated of under the two headings. There is, in short, but one science of chemistry, and the separate consideration of the chemistry of the majority of the compounds of carbon is, to a large extent, a matter of convenience only. The very great number of the compounds of carbon and the complexity of many of them, together with the general readiness which they usually exhibit to enter into new combinations, may be mentioned as amongst the reasons for their separate study. The one fundamental fact concerning every so-called organic compound is, that it contains carbon as one of its constituents, combined with one or more other elements; but, as we have already seen, every compound of carbon is not an organic compound in any sense which it is convenient strictly to define. Of course, so old and historically interesting a term as *organic chemistry* will continue to be used; and there is no objection to such use, provided students remember that when the term is used, it is only conventionally and not etymologically accurate.

It will be unnecessary to discuss again in what follows the chemistry of those compounds of carbon which have already been treated of in earlier parts of the Manual.

As instances of the formation, from purely inorganic materials (or from products obtainable from inorganic materials), of compounds which are generally classed as organic, the following may be mentioned:—

(1) The formation of acetylene, C_2H_2, by passing electric sparks from carbon terminals in an atmosphere of hydrogen; and by the action of water on calcium carbide.

(2) The formation of potassium cyanide, KCN, by passing nitrogen over a strongly-heated mixture of potassium and carbon, or of potassium carbonate and carbon heated to the temperature at which potassium is liberated (p. 68).

(3) The formation of marsh gas, CH_4, by passing a mixture of hydrogen sulphide and vapour of carbon bisulphide over red-hot copper.

(4) The formation of urea, $CO(NH_2)_2$, by the action of ammonia on carbonyl chloride (phosgen); and by evaporating to dryness a solution of ammonium cyanate.

(5) The formation of potassium formate, $KHCO_2$, by the action of carbonic oxide on potassium hydroxide.

Elements which enter into the composition of Organic Substances.—The elements which, besides carbon, are of the greatest importance from their entering most frequently into the composition of organic substances are hydrogen, oxygen, and nitrogen. All the naturally occurring organic substances contain carbon and hydrogen, associated almost always with oxygen, and often with nitrogen; some of them also contain sulphur or phosphorus or both, in small quantity Amongst artificially prepared organic substances, compounds have been obtained containing almost any of the other known elements.

Detection of the various elements present in Organic Substances.—It is not intended to give here any detailed account of the analysis of organic substances, but the general principles and a few important methods may advantageously be outlined.

In order to demonstrate the presence of combined carbon and hydrogen in an organic substance, it is usual to burn a small quantity of the substance in a current of pure dry air or oxygen in a hard-glass tube closely packed for a part of its length with cupric oxide which is kept red-hot throughout the operation. The current of air or oxygen enters at one end of the tube and the gaseous products of combustion pass out at the other. During the process the carbon and hydrogen of the substance are completely oxidized—the former into carbonic anhydride and the latter into water—and the presence of the two elements is indicated by the formation of these respective products. This process can be made a method of quantitative analysis, since, by collecting and determining the weights of the two products obtainable from a known weight of the organic substance, data are obtained from which the proportions by weight in which the two elements are present in the substance can be calculated.

The presence of nitrogen in an organic substance is detected by strongly heating a few grains of the substance in a test-tube with a small piece of metallic sodium, grinding up the fused mass with water, filtering, and examining the solution for the presence of a dissolved cyanide. In the process the nitrogen of the substance, along with some of the carbon, combines with the sodium to form sodium cyanide, NaCN ; and the observation that a cyanide has been formed is a proof of the presence of nitrogen in the substance. Part or the whole of the nitrogen of some (but not of all) organic substances is evolved as ammonia when the substance is moderately heated in a test-tube with soda-lime.* The quantitative determination of nitrogen is effected by various methods, but the only one which need be mentioned here is analogous to that employed for the determination of carbon and of hydrogen. A weighed quantity of the substance is heated in a slow current of carbonic anhydride in a glass tube containing cupric oxide which is heated red-hot. The nitrogen is liberated either as such, or in the form of gaseous oxides of nitrogen. Before emerging from the tube the mixture of gases passes over a quantity of red-hot copper wire-gauze, tightly packed. The latter retains any free oxygen by combining with it to form cupric oxide, and also decomposes the oxides of nitrogen, similarly retaining the oxygen of these while the liberated nitrogen passes on. The carbonic anhydride, water vapour, and nitrogen which emerge are passed into a graduated tube containing a concentrated solution of potassium hydroxide. The carbonic anhydride is here absorbed forming potassium carbonate, the water vapour condenses to form liquid water, and the pure nitrogen is collected and its volume is measured. From the observed volume, under the conditions of temperature and of pressure which have also been noted, the weight of the evolved nitrogen can be calculated.

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* The product obtained by slaking quicklime with a solution of sodium hydroxide.

The presence of oxygen in a non-volatile organic substance can usually be detected by simply heating the dry substance in an atmosphere free from oxygen, and observing the formation of water. The oxygen necessary for the production of water, in such a case, must have been present in the substance under examination. The direct quantitative determination of oxygen presents considerable experimental difficulties, and no satisfactory method for making this determination has come into general use. It is usual in actual practice to determine the quantities of all the other elements present in a given weight of the substance and then to regard the remainder as the quantity of oxygen.

In order to detect sulphur or phosphorus in an organic substance, the latter is, in most cases, first oxidized by some suitable process, and the oxidation products are then examined for the presence of sulphuric or phosphoric acid. The quantitative determination of these elements also usually requires oxidation as a preliminary.

The detection and quantitative determination in organic substances of other elements, sueh as chlorine, bromine, iodine, metals, etc., require in general the oxidation of the substance or the decomposition of it by some other process, and the subsequent examination of the products of such operations by the methods of qualitative and quantitative analysis applicable to inorganic substances.

General effects of Heat upon Organic Substances.—The effects produced by heating various organic substances vary greatly in the cases of different compounds. We shall briefly consider the general effects (1) when organic substances are heated by themselves, that is, out of contact with anything more than small quantities of air; and (2) when they are heated with free access of air.

(1) Solid organic substances when heated may simply

become liquid, and the liquid so produced may, on being further sufficiently heated, boil and be completely volatilized without undergoing any decomposition. Glacial acetic acid and acetamide are examples of such substances. Other solid substances may similarly become liquid, but the liquid on further heating may decompose before the temperature of volatilization has been reached. This is the case with cane sugar and with urea. Other solid substances again, such as starch and cellulose, cannot be liquefied by heating them because the temperature at which decomposition takes place lies below the temperature of liquefaction. Substances belonging to these last two classes very commonly yield on decomposition by heat a quantity of volatile products (some of which are gaseous and others liquid at ordinary temperatures) and leave behind in the vessel in which the decomposition has taken place, a highly carbonaceous, non-volatile black residue or charcoal. Charcoal suitable for special purposes is often prepared by thus heating starch, sugar, cellulose, etc. When non-volatile organic substances are subjected to this treatment the process is called *dry* or *destructive distillation.* Such processes are carried out on a very large scale with wood, with coal, and with different kinds of shale, and form a part of several important manufacturing industries.

Of organic substances which are liquid at ordinary temperatures, a very large number, such as common alcohol and ether, are capable of volatilization without decomposition, while others, such as glycerin, decompose at temperatures below their boiling points. Substances which belong to this latter class cannot therefore be distilled without decomposition, at least under ordinary pressures. In some instances it is found possible, by diminishing the pressure inside the distilling apparatus, to lower the boiling point of the liquid to a temperature below that at which decomposition takes place and so to ensure its distilling undecomposed.

Organic substances which are gases at ordinary temperatures, and the vapours of organic substances which are solids or liquids under these circumstances but which volatilize undecomposed, may be exposed to the action of high temperatures by slowly passing them through heated tubes. Under this treatment some decompose readily, while others do not undergo any, or at least any considerable, change. A method frequently made use of for very rapidly heating a vapour, is that employed in the manufacture of "oil gas" from paraffin oil. The liquid oil is allowed to drop on a red-hot metal or brick surface, when the vapour which is at first produced becomes very strongly heated before it has time to diffuse away from the hot surface. In this way the paraffin oil is decomposed, yielding some coke and combustible gases which do not become liquid again at ordinary temperatures. This operation is technically called "cracking" the hydrocarbons of which the paraffin oil is composed.

(2) When organic substances are strongly heated in suitable forms of apparatus with free access of air, they usually undergo complete oxidation, so far, at least, as their carbon and hydrogen are concerned. These elements become converted into carbonic anhydride and water respectively. When a salt of any of those organic acids which contain carbon, hydrogen, and oxygen only, is subjected to this treatment, the carbon may either be completely driven off as carbonic anhydride, or a part may remain combined in the form of a carbonate. The metal of the salt may remain behind either as metal (silver, platinum, etc.) or as oxide (lead oxide, zinc oxide, ferric oxide, etc.) or as carbonate (potassium carbonate, barium carbonate, etc.).

Distillation.—The purification of organic substances is often effected by distillation, as, for example, when a volatile substance is impure from the presence of any non-volatile admixture. The separation of alcohol by distillation from the non-volatile constituents present in the liquid of the fermenting tun is an instance of this kind (p. 485).

A mixture of two or more liquids (all of them volatile, but of different boiling points when pure and unmixed) may be more or less completely separated by "*fractional distillation*"—that is, by separately collecting the portions of the distillate ("fractions" as they are called) which distil at different temperatures, or rather, within certain intervals of temperature. Such fractions do not, as a rule, consist entirely of one single liquid, but generally contain some of the other volatile substances present in the original mixture. By subjecting each original fraction to a second fractional distillation, and systematically carrying out the same process on succeeding fractions for several times, fractions of almost constant boiling point, and composed almost entirely of one liquid can in many instances be obtained; but in some cases nothing more than a very partial separation can be effected. Thus from a mixture of alcohol and water it is not possible, by distillation alone, to obtain alcohol containing less than about 5 per cent. of water.

Classes of Organic Compounds.—The majority of organic compounds are conveniently grouped into two main classes, which are known as the Fatty (or Aliphatic), and the Aromatic classes respectively. When these names were first employed, only a comparatively limited number of organic compounds were known. The natural fats gave rise to a number of representatives of the first class, which may all be regarded as derivatives of methane, CH_4; a considerable number of representatives of the second class, which may be regarded as derivatives of benzene, C_6H_6, are more or less aromatic substances, such as some of the essential oils, etc. The words fatty and aromatic are of historical interest, but although in common use, they cannot now be looked upon as very appropriate. In dealing with the fatty or aliphatic and the benzene or aromatic compounds, these two classes will only be considered separately in so far as a moderately systematic treatment may seem to require.

Constitution or Structure of Organic Compounds.—The problem of the relations to one another of the various atoms which compose a molecule, is one which early attracted the interest and attention of chemists; and it is one for the solution of which materials have been accumulated slowly and laboriously from the synthetical and analytical investigation first of the simpler and afterwards of the more complex chemical compounds, inorganic and organic. How to recognise the presence of certain groups of atoms, or radicals, in the molecules of chemical substances, and how to find out the position of these groups in the molecules is often a most difficult and yet a most fascinating task for the enthusiast and skilled experimentalist in chemistry; and how to so marshal these groups (drawn perhaps from several different sources, and obtainable only in a state of combination) that he shall produce by art the compound originally only furnished by nature, is still more difficult, but also more fascinating. More fascinating firstly, because it will furnish proof that his synthetical work was sound; secondly, because by artificially and perhaps cheaply producing a rare colour, a rare perfume, a rare flavour, or a previously costly medicine, he may become a benefactor to his fellow-man; and thirdly, because he may gain the honour of unveiling for all time one more of the truths of nature.

In practically attacking the problem of the constitution of a compound, the chemist proceeds to note whether the substance is acid, alkaline, or neutral; to act on it with a base of known constitution if it is an acid, or with an acid of known constitution if it is a base, and to analyse the produced salts; to oxidize it; to deoxidize it; to heat it; to electrolyse it; to chlorinate it; to remove or add hydroxyl (OH), carbonyl (CO), etc.; to substitute hydrogen by a compound radical, and *vice versâ;* and, generally, to perform many such operations, in the hope that the lines of chemical cleavage in the molecule will be detected, the essential groupings of atoms in the molecule be discovered, and even the positions of atoms or groups of atoms in relation to each other be reasonably inferred. Briefly, similarity in properties implies similarity in constitution or structure. *Per contra,* similarity in structure being reasonably implied, reference to properties shows whether or not the reason is on the right track towards truth in the matter of constitution or structure, the advance towards error being prevented and towards truth being maintained whatever be the result of the reference, new truths not infrequently being unveiled. Thus, by the way, in chemistry, do fact and theory ever discharge their obligations to each other.

Notation of Organic Compounds.—In order that we may convey to one another our conclusions respecting the constitution of organic compounds, notation has to be carried somewhat farther in organic than is as a rule necessary in inorganic chemistry. The relative positions of atoms and groups of atoms in a molecule may be indicated by placing the symbolic letters above or beneath one another as well as on one line, and the quantivalence of atoms, as well as the ways in which we conclude they are linked in the molecule, may be indicated by lines (— = or ≡) or dots (. : ⋮) either completely or only partially employed throughout the formula; each dot or line or "link," or "bond," representing the supposed condition of union between two neighbouring atoms or radicals. Formulæ which, by the aid of such dots or lines, purport to represent the relative positions of the atoms and groups of atoms in molecules (*i.e.*, to represent the constitution or structure of the molecules) are called *constitutional* or *structural formulæ*. Many examples of such formulæ will be met with in the succeeding pages of this Manual. When structural formulæ are written in the most extended form, so as to represent by the aid of lines the way in which every atom in a molecule is united to its adjacent atoms, the resulting formulæ are often called *graphic* formulæ.

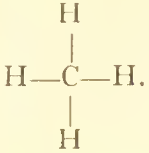
QUESTIONS AND EXERCISES

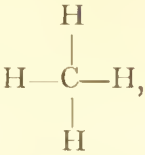
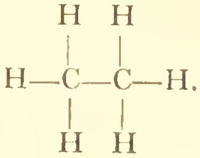
What do you understand by organic chemistry?—Give methods of ascertaining the presence of carbon, hydrogen, and nitrogen in organic compounds.—Give an outline of the methods by which the quantities of carbon, hydrogen, oxygen, and nitrogen are determined in organic compounds.—What is meant by "fractional" distillation? —Name two of the chief classes into which organic compounds are divided.—How is the constitution of an organic compound ascertained? —What do you understand by constitutional or structural formulæ? —What are graphic formulæ?

HYDROCARBONS

Compounds known as hydrocarbons contain the elements hydrogen and carbon only, and are exceedingly numerous. A very large number of the known hydrocarbons belong to the fatty class, three of the chief groups being the Paraffin, the Olefine, and the Acetylene series.

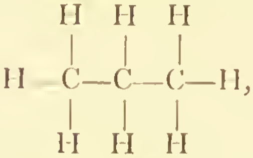
THE PARAFFIN SERIES OF HYDROCARBONS

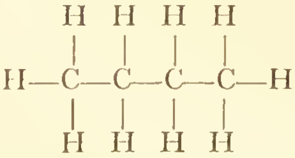
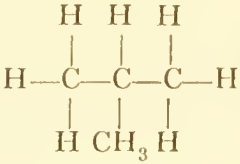
Of all the known hydrocarbons, the simplest in composition is methane or marsh gas, which is the first member of the series called Paraffins. In this series of hydrocarbons (and in it alone) the total combining capacity of each carbon atom is satisfied in such a manner (either by linkage with hydrogen atoms, or with other carbon atoms, or, as is almost always the case, by linkage, partly with hydrogen atoms and partly with other carbon atoms) that the members of the series are not capable of entering into direct union with chlorine or bromine, so as to form addition compounds. Hence the series of paraffins is often called the series of *saturated* hydrocarbons. Methane is the only hydrocarbon which has the total combining capacity of its carbon satisfied by linkage with hydrogen atoms. Its composition is represented by the formula CH_4 or  $\begin{array}{c}\mathrm{H}\\ | \\ \mathrm{H—C—H.}\\ | \\ \mathrm{H}\end{array}$

If we suppose one hydrogen atom of methane to be removed and its place to be taken by the group $—CH_3$ (which is called methyl), we get the composition of the next simplest paraffin, ethane, C_2H_6. There is no reason to suppose that any one of the four hydrogen atoms of methane differs in the least from any of the others in the way in which it is related to the carbon atom and to the other three hydrogen atoms. Thus on considering in the graphic formula  $\begin{array}{c}\mathrm{H}\\ | \\ \mathrm{H—C—H}\\ | \\ \mathrm{H}\end{array}$, the relations of any particular hydrogen atom, we see that it is linked to a carbon atom which in turn is linked to three other hydrogen atoms. Accordingly it is immaterial which of the four hydrogen atoms we suppose to be replaced by the methyl group, because, if the relations of all four are similar, there would in any case result the substance ethane,  $\begin{array}{cc}\mathrm{H}\ \ \mathrm{H}\\ |\ \ \ | \\ \mathrm{H—C—C—H.}\\ |\ \ \ | \\ \mathrm{H}\ \ \mathrm{H}\end{array}$

Ethane is also a paraffin (the second of the series) and contains two carbon atoms, each of which is linked one-fourth to carbon and three-fourths to hydrogen.

But just as in methane any one of the four hydrogen atoms is related to the single carbon atom in the same way as any other, so in ethane, any one of the six hydrogen atoms is related to one of the carbon atoms in the same way as any other is.

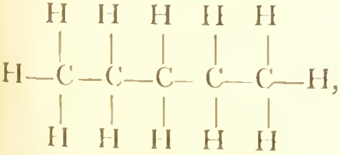
Thus on considering, in the graphic formula for ethane just given, the relations of any one of the six hydrogen atoms, we see that it is linked to a carbon atom which is in turn linked to two other hydrogen atoms and to the group —CH_3. The relation of each hydrogen atom to what is called the "carbon nucleus," in this case C—C, is the same. Hence if we suppose one hydrogen atom of ethane to be removed and its place to be taken by the group —CH_3, it is immaterial in this case also which of the hydrogen atoms we suppose to be thus replaced. The resulting compound is propane, C_3H_8, the third hydrocarbon of the paraffin series. Consideration of the graphic formula of this substance,  $\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$, reveals the fact, however, that all of the hydrogen atoms are no longer similarly related to the carbon nucleus, C—C—C. Each hydrogen atom is linked to a carbon atom as before, but while six of the hydrogen atoms are linked to the two end carbon atoms, which besides are one-fourth linked to carbon, the two remaining hydrogen atoms are linked to the central carbon atom which is one-half linked to carbon. The eight hydrogen atoms in propane are thus divisible into two groups, consisting of six and of two respectively, according to the position in the carbon nucleus of the carbon atoms to which they are linked. If then, we suppose one hydrogen atom of propane to be removed, and its place to be taken by the group —CH_3 it *may* not any longer be immaterial which atom we suppose to be thus replaced. The resulting compound will in any case have the composition, C_4H_{10}, but it is evident that two different arrangements of these atoms are possible as indicated by the formulæ :—

(1)  $\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$ and (2)  $\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & CH_3 & & H & & \end{array}$. The formula (1) would represent the arrangement in the case of the replacement of an end hydrogen atom of propane by —CH_3; the formula (2) that in the case of the similar replacement of a central hydrogen atom. As a matter of fact, two (and only two) paraffins are known, both with

molecular weight corresponding to the formula, C_4H_{10}, but differing from each other in properties. The formula (1) is assumed to represent one of these two compounds which is called normal butane, and the formula (2) to represent the other which is called isobutane.

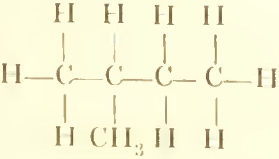
Although it is beyond our present intention to follow much further the possible varieties in the constitution of the compounds which we may regard as derived from "lower" paraffins (*i.e.*, paraffins containing in their molecules a smaller number of carbon atoms) by the replacement in these of different hydrogen atoms by the methyl group; it may be well to proceed here one step further in this direction in the cases of normal butane and isobutane, both of which we may regard as derived, by this kind of replacement, from propane.

Thus on considering the hydrogen atoms of normal butane (formula (1) above) it is seen that six of them (the two end sets of three each) are linked to two carbon atoms which in turn are one-fourth linked to carbon and are both related in the same way to the carbon nucleus, while the remaining four (the two central sets of two each) are linked to carbon atoms which in turn are one-half linked to carbon and are both related in the same way to the carbon nucleus, but that any one of the six has got the same kind of relations to the remaining atoms in the molecule as any other of the six has, and that any one of the four has likewise got the same kind of relations to the remaining atoms in the molecule as any other of the four has. From normal butane then, if we suppose one hydrogen atom to be replaced by the methyl group, it is conceivable that two different substances might be derived, one of which would be represented by the formula



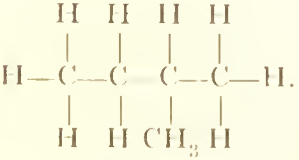
$$\begin{array}{ccccccccccccc}
 & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\
 & & | & & | & & | & & | & & | & & \\
\mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H}, \\
 & & | & & | & & | & & | & & | & & \\
 & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & &
\end{array}$$

and the other by the formula



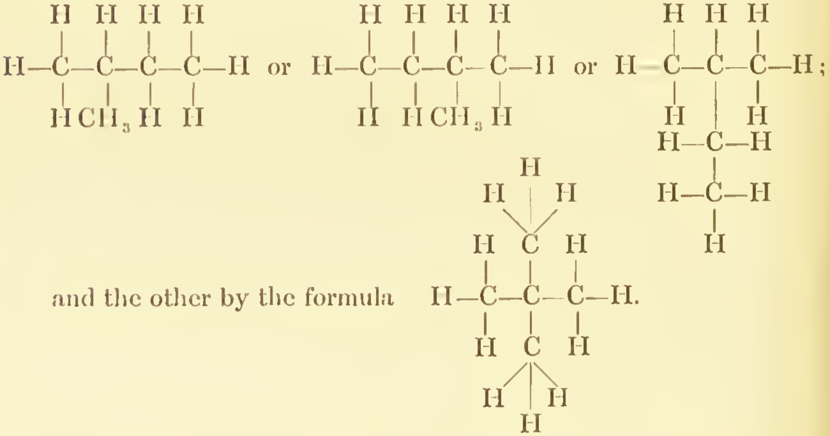
$$\begin{array}{ccccccccccc}
 & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\
 & & | & & | & & | & & | & & \\
\mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\
 & & | & & | & & | & & | & & \\
 & & \mathrm{H} & & \mathrm{CH_3} & & \mathrm{H} & & \mathrm{H} & &
\end{array}$$

or



$$\begin{array}{ccccccccccc}
 & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\
 & & | & & | & & | & & | & & \\
\mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H}. \\
 & & | & & | & & | & & | & & \\
 & & \mathrm{H} & & \mathrm{H} & & \mathrm{CH_3} & & \mathrm{H} & &
\end{array}$$

But on considering the hydrogen atoms of isobutane (formula (2) above) it is seen that nine of them (three sets of three each) are linked to three carbon atoms which in turn are one-fourth linked to carbon and are all related in the same way to the carbon nucleus, while the remaining one is linked to a carbon atom which in turn is three-fourths linked to carbon and differs from all the others in its relation to the carbon nucleus. The relations to the remaining atoms in the molecule, of any one of the series of nine hydrogen atoms are of exactly the same kind as those of any other of them, and the relations of each of them are different from those of the single hydrogen atom. Here again then, if we suppose one hydrogen atom of isobutane to be replaced by the methyl group, it is conceivable that two different substances might be derived, of which one would be represented by the formula—



or or ;

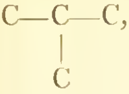
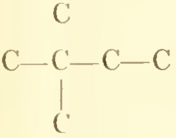
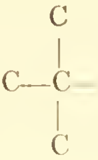
and the other by the formula .

But comparison of the formula given for the second of the conceivable derivatives from normal butane with that given for the first of the conceivable derivatives from isobutane shows that these two are identical, and that therefore there are theoretically only three paraffins of the formula C_5H_{12} derivable from the two butanes by the replacement of one hydrogen atom by the group —CH_3. As a matter of fact three paraffins (and only three) are known all with molecular weight corresponding to this formula. They are called pentanes and they differ very considerably from one another in their properties.

Isomerism, Polymerism, Metamerism.—The occurrence of two or more substances possessing the same centesimal composition but differing in properties, as exemplified in the cases of a number of the paraffins mentioned in the foregoing paragraphs, is very frequently met with, especially in organic chemistry. Substances which stand in this relationship to each other are termed *isomeric* (from ἴσος, *isos*, equal, and μέρος, *meros*, part); and their condition is spoken of as one of *isomerism*. There is sometimes good reason for doubling or otherwise multiplying the formula of one of two *isomers*, *isomerides*, or isomeric substances. Thus a molecule of ethylene (olefiant gas), one of the chief illuminating constituents of coal gas, is represented by the formula C_2H_4, while a molecule of butylene, a hydrocarbon having the same percentage composition as olefiant gas, is represented by the formula C_4H_8, because butylene in the state of gas is specifically twice as heavy as ethylene, and must contain, therefore, in each molecule, twice as many atoms, since (Avogadro) equal volumes of the substances in the gaseous state and under the same conditions contain equal numbers of molecules; its formula is, consequently, fixed in conformity with these facts. This variety of isomerism is termed *polymerism* (from πολὺς, *polūs*, many or much, and μέρος, part). Formaldehyde, CH_2O, acetic acid, $C_2H_4O_2$, and lactic acid, $C_3H_6O_3$, furnish another group illustrative of polymerism. Metastannic acid (*see* p. 216) is a polymeric variety (*polymer* or *polymeride*) of stannic acid. An example of another variety of isomerism is seen in the case of ammonium cyanate and urea, substances already alluded to in connection with cyanic acid. These and several other pairs of chemical substances have dissimilar properties, yet are similar in the centesimal proportion of their elements, and we cannot avoid the conclusion that each molecule possesses the same number of atoms. But the reactions of these substances indicate their probable constitution; and this is represented in their formulæ by the disposition of the symbols. Thus ammonium cyanate is represented by the formula NH_4CNO, urea by $CO(NH_2)_2$. Such substances are termed *metameric* (from μετά, *meta*, a preposition denoting change, and μέρος), and their condition spoken of as one of *metamerism*. Ethyl acetate (p. 165) is metameric with butyric acid (p. 526); they have the same percentage composition and the same vapour density and each might be represented by the formula $C_4H_8O_2$; but their properties warrant us in assuming that their atoms occupy different positions in the two molecules—justify us in writing $CH_3{\cdot}COOC_2H_5$ as the formula for a molecule of ethyl acetate, and $C_3H_7{\cdot}COOH$ as the formula for a molecule of butyric acid. Methyl acetate, $CH_3{\cdot}COOCH_3$, propionic acid, $C_2H_5{\cdot}COOH$, and ethyl formate, $H{\cdot}COOC_2H_5$, are isomers of the metameric variety, or *metamers* or *metamerides;* also quinine and quinidine, cinchonine and cinchonidine, many of the volatile oils, etc.

Homologous Series.—In the consideration, so far, of the series of paraffins, we have seen that, starting from the first member, methane, each succeeding member of the series differs from the one which immediately precedes it by containing the group $—CH_3$ in the place of an atom of hydrogen; or, in other words, by the common difference of one atom of carbon and two atoms of hydrogen (CH_2). Many other series of substances besides the paraffins are known in which the successive members differ from one another by CH_2, or a multiple of CH_2. Such series are called *homologous* (from ὁμὸς, *homos*, the same, and λόγος, *logos*, proportion). The "higher" members of the paraffin series (*i.e.*, those containing in their molecules more than one atom of carbon) are called *homologues* of methane.

General formulæ for homologous series.—It is often convenient (and it is always possible) to represent the general composition of the members of any homologous series of compounds by means of a formula. In the case of the paraffins the general formula is usually written C_nH_{2n+2}, where n represents the number of carbon atoms in a molecule of the compound. This formula shows that whatever number of carbon atoms a molecule of the paraffin contains, it contains twice that number of hydrogen atoms and two hydrogen atoms besides. The general formulæ for some other homologous series will be given later in their respective places.

Normal Paraffins.—The term *normal* is applied to those paraffins in which the carbon nucleus is capable of being represented as consisting of carbon atoms so linked together as to form a single "chain" without any "side-branches" (or "side-chains"); for example, C—C as in ethane, C—C—C as in propane, C—C—C—C as in normal butane, C—C—C—C—C as in normal pentane. It will be observed that in these "chains" the carbon atoms are represented as either one-fourth or one-half linked to other carbon atoms, but never more than this. Contrast these straight "chains" with  $\begin{array}{ccccc} C & - & C & - & C \\ & & | & & \\ & & C & & \end{array}$, the carbon nucleus of isobutane, and with  $\begin{array}{ccccccc} C & - & C & - & C & - & C \\ & & | & & & & \\ & & C & & & & \end{array}$ and  $\begin{array}{ccccc} & & C & & \\ & & | & & \\ C & - & C & - & C \\ & & | & & \\ & & C & & \end{array}$, those of isopentane and of tetramethyl methane respectively, in the first two of which one carbon atom of each is represented as three-fourths, while in the last, one carbon atom is represented as wholly linked to other carbon atoms. Carbon atoms which may thus be distinguished in the carbon nucleus by the different proportion of their combining capacity which is satisfied by linkage with other carbon atoms, are designated as primary, secondary, tertiary, or quaternary, according as one-fourth, one-half, three-fourths, or the whole of that combining capacity is so satisfied.

In connection with these designations of carbon atoms it is not unimportant to note that the carbon atom in methane is not linked to other carbon atoms at all but to hydrogen atoms exclusively; and that, with respect to this peculiarity of its carbon atom, methane is quite exceptional and differs from all other hydrocarbons.

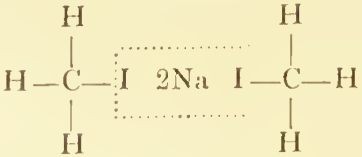
Occurrence of Paraffins in Nature.—Methane or marsh gas occurs as a product of the slow decay of vegetable matter in presence of much water, as, for example, in stagnant pools, marshy places, etc., and also as the "fire-damp" of coal mines. Further, methane and several of its homologues are present in the gases which issue from the earth in the petroleum region of Pennsylvania and in other parts of the world; while the crude petroleum itself which flows, or is pumped, from the earth in these places, also consists of or contains higher members of the series.

Formation of Paraffins in the dry distillation of coal, wood, shale, etc.—The volatile products obtained by the dry distillation of these substances always contain considerable quantities of paraffins. Thus methane is a constant constituent, in large proportion, of coal gas and of wood gas. Further in the dry distillation of shale in the Scottish "paraffin oil" industry, besides the paraffins which are contained in the gaseous products, the liquid distillate consists largely of liquid paraffins in which solid compounds, also belonging to the paraffin series, are held in solution.

Methods for the preparation of Paraffins.—It may now conveniently be shown that the process discussed on pp. 433-436 of building up, from one member of the paraffin series, the next higher member, by the replacement of a hydrogen atom by the methyl group, is in certain instances capable of actual experimental realization. This synthesis can be effected by several different methods, and one or two of these methods may be described here with some detail.

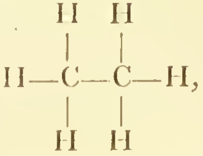
1. One hydrogen atom of methane can, without difficulty, be replaced by chlorine, methyl chloride, CH_3Cl, being produced (p. 457). From methyl chloride the corresponding iodine compound (methyl iodide, CH_3I) could be obtained. One way to do this would be to convert the methyl chloride into methyl alcohol, CH_3OH (p. 482), and from this to prepare methyl iodide. It is indeed usual to prepare methyl iodide from methyl alcohol (p. 459), but methyl alcohol is prepared on the large scale by other methods (p. 483) very much more easily and cheaply than would be possible if it had to be obtained from methane by way of methyl chloride. This method is stated here, however, in order to show that the end in view, viz., the preparation of methyl iodide starting from marsh gas, is capable of attainment.

If methyl iodide, however prepared, is dissolved in a suitable solvent, such as ether, and the solution is treated with metallic sodium, a reaction takes place which may be diagrammatically represented thus :—



$$\begin{array}{ccccccc} & H & & & & H & \\ & | & & & & | & \\ H- & C & -I & 2Na & I- & C & -H \\ & | & & & & | & \\ & H & & & & H & \end{array}$$

The products are, sodium iodide (2NaI) and ethane,



$$\begin{array}{cccc} & H & H & \\ & | & | & \\ H- & C- & C- & H, \\ & | & | & \\ & H & H & \end{array}$$

and the mode of its formation here furnishes strong evidence concerning the constitution of ethane.

By carrying out a series of operations analogous to those described in the case of methane, only starting from ethane instead, it is possible to prepare a derivative from this latter hydrocarbon also, in which the place of one atom of hydrogen is taken by iodine so as to form ethyl iodide, C_2H_5I. On the large scale ethyl iodide is, however, always prepared from ethyl alcohol, C_2H_5OH (p. 459) in the same way that methyl iodide is prepared from methyl alcohol. If ethyl iodide is dissolved in pure ether and the solution is treated with metallic sodium, a reaction takes place which is exactly analogous to that represented above with methyl iodide :—

$$CH_3CH_2\,I \quad 2Na \quad I\,CH_2CH_3,$$

whereby normal butane is produced; while if the operation is similarly carried out, but with the employment of a mixture of methyl and ethyl iodides instead of ethyl iodide alone, besides ethane and normal butane (which may both be supposed to be formed according to the actions already represented above), a quantity of a third paraffin, propane, C_3H_8, is always produced. The formation of this paraffin may be represented thus :—

$$CH_3\,I \quad 2Na \quad I\,CH_2CH_3.$$

Besides by the method already described for obtaining normal butane from ethyl iodide by the action of sodium, this paraffin can also be prepared (mixed, however, with ethane and normal hexane, C_6H_{14}), by a method strictly analogous to that just given above for the preparation of propane, only employing a mixture of methyl iodide and normal propyl iodide, C_3H_7I,* instead of the mixture of methyl and ethyl iodides.

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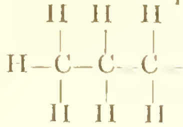
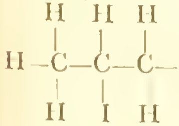
* Two iodides are known, both with molecular weight corresponding to the formula C_3H_7I. They are called normal and iso-propyl iodides, and may be represented by the formulæ 

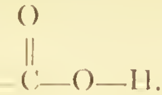
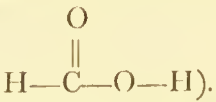
$$\begin{array}{ccccccc} & & H & & H & & H \\ & & | & & | & & | \\ H & - & C & - & C & - & C & - & I \\ & & | & & | & & | \\ & & H & & H & & H \end{array}$$

and 

$$\begin{array}{ccccccc} & & H & & H & & H \\ & & | & & | & & | \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & I & & H \end{array}$$

respectively.

Thus by two variations of the same method, *i.e.*, by acting with sodium (*a*) upon solution of a single iodide, and (*b*) upon mixed solutions of two different iodides, normal paraffins can be obtained either with even numbers of carbon atoms in their molecules, or with odd numbers (greater than one). It must be noted, however, that when mixed iodides are employed, a mixture of three different paraffins is always obtained, as illustrated above, and even the approximate separation of these from one another may not be practicable. A reaction of this kind cannot, therefore, be employed as a mode for preparing a single paraffin in a state of purity.

2. Paraffins are obtained (along with other products) by the electrolysis of solutions of potassium salts of the homologous series of acids to which acetic acid belongs. These acids are all regarded as containing a group of atoms which is called the *carboxyl* group and is supposed to consist of a carbon atom with its combining capacity three-fourths satisfied by linkage with two oxygen atoms (*i.e.*, one-half by linkage with one oxygen atom, which is thereby fully satisfied, and one-fourth by linkage with a second oxygen atom which, in turn, is further linked to a hydrogen atom). The constitution of this group may be represented graphically thus:  $-\overset{\displaystyle O}{\overset{\|}{C}}-O-H$. To save space, however, it is often printed —COOH. In the acids of the acetic series (and in carboxyl acids generally) the carbon atom of this carboxyl group is supposed to be further one-fourth linked to another carbon atom in the molecule (with the single exception of formic acid, the first member of the acetic series, in which the carbon atom of the carboxyl group is the only one contained in the molecule and is supposed to be further one-fourth linked to a *hydrogen* atom thus:  $H-\overset{\displaystyle O}{\overset{\|}{C}}-O-H$).

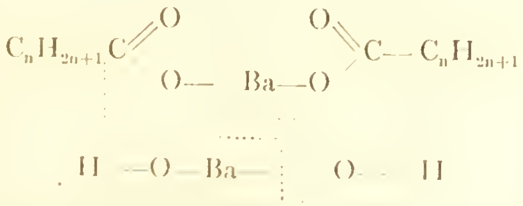
The composition of any member of the acetic series of acids may be represented by the general formula $C_nH_{2n}O_2$, or better by the more extended formula $C_nH_{2n+1}COOH$. The consideration of this latter mode of writing the general formula for these acids shows that the acids themselves may be regarded as paraffins (C_nH_{2n+2}) from which one hydrogen atom has been removed (leaving C_nH_{2n+1}), the place of this hydrogen atom being taken by the carboxyl group. It is in this light that we shall regard these acids for our present purpose.

The formation of various paraffins by the electrolysis of solutions of the potassium salts of acids of the acetic series may be illustrated by the following example :—

When a concentrated solution of potassium acetate, CH_3COOK, is electrolysed, it may be represented that the salt is first separated into potassium and the acid radical of the acetates and that other changes follow. Thus there are formed :

At the Cathode K	At the Anode CH_3COO
which interacts with water, yielding KOH and H. The H atom then unites with another H atom, similarly produced, to form a hydrogen molecule, H_2.	which breaks up for the most part into $-CH_3$ and CO_2 (although other changes occur to some extent). Each $-CH_3$ group then unites with another $-CH_3$ group, similarly produced, to form an ethane molecule, C_2H_6.

3. Another method for the preparation of paraffins, which is of somewhat general applicability, consists in heating the salts of the acids of the acetic series with basic hydroxides. The basic hydroxide, at a high temperature, removes carbon and oxygen from the salt in the proportions in which these elements combine to form carbonic anhydride, a carbonate and a paraffin resulting from the interaction. It has been found that the best results, on the whole, are obtained by employing the barium salts and heating these with barium hydroxide. Writing the general formula for the barium salt (in which the bivalent atom of barium must of course be represented as taking the places of two hydrogen atoms, *i.e.*, of one each in two molecules of the acid) the change which occurs may be represented diagrammatically as follows :—



or by an equation as follows :—

$$(C_nH_{2n+1}COO)_2Ba + Ba(OH)_2 = 2BaCO_3 + 2C_nH_{2n+2}$$

METHANE. *Marsh gas. Light carburetted hydrogen. Methyl hydride. Fire-damp.* CH_4.—This gaseous hydrocarbon may be made from its elements by combining the carbon with sulphur to form carbon bisulphide and the hydrogen with sulphur to form hydrogen sulphide, and then passing these two compounds over red-hot copper. It occurs naturally in coal mines and in the mud-volcanoes of the Crimea; it is frequently associated with the crude petroleum that issues from the earth, and, mixed with carbonic anhydride and nitrogen, is constantly rising in bubbles to the surface of stagnant pools in marshy places. It is a non-illuminating constituent of ordinary coal gas. It may be prepared by heating a mixture of 2 parts of dry sodium acetate, 3 of lime, and 2 of caustic soda or, better, caustic potash.

$$\underset{\text{Sodium acetate}}{CH_3{\cdot}CO{\cdot}ONa} + \underset{\text{Caustic soda}}{NaOH} = \underset{\text{Methane}}{CH_4} + \underset{\text{Sodium carbonate}}{Na_2CO_3}$$

Methane prepared in this way is never quite pure, but is mixed with other gases of which the principal ones are hydrogen and ethylene (p. 452). Pure methane is obtainable by the action of water on zinc methide, $Zn(CH_3)_2$:—

$$Zn(CH_3)_2 + 2H_2O = Zn(OH)_2 + 2CH_4$$

Methane is a colourless and odourless gas of sp. gr. 8·07. It only dissolves to a small extent in water but is rather more soluble in alcohol. It can be condensed to the liquid state by the application of a moderate pressure at a very low temperature. It burns in air, but, when pure, with a practically non-luminous flame : $CH_4 + 2O_2 = CO_2 + 2H_2O$.

Mixtures of methane and air in suitable proportions give rise to violent explosions when fired. This occurs occasionally in insufficiently ventilated coal mines. About ten times its volume of air are required for the complete combustion of any given volume of methane. When methane is mixed with eighteen times its volume of air (or more than this) the mixture does not explode on the application of a light.

ETHANE, C_2H_6. *Dimethyl. Ethyl hydride.*—This is one of the constituents of crude petroleum. It is usually prepared in quantity by the electrolysis of a concentrated solution of potassium acetate (p. 443). The mixture of ethane and carbonic anhydride which is given off at the positive electrode during this process is made to bubble through a concentrated solution of potassium hydroxide which absorbs the carbonic anhydride, while the ethane passes on unabsorbed.

Ethane is also obtained (*a*) by the action of sodium upon methyl iodide dissolved in ether (p. 440), $2CH_3I + 2Na = 2NaI + C_2H_6$; (*b*) by the action of water upon zinc ethide, $Zn(C_2H_5)_2 + 2H_2O = Zn(OH)_2 + 2C_2H_6$; and (*c*) by the interaction of zinc methide and methyl iodide: $Zn(CH_3)_2 + 2CH_3I = ZnI_2 + 2C_2H_6$.

Ethane is, like methane, a colourless and odourless gas, Its sp. gr. is 14·95. Water dissolves less than one tenth of its volume of ethane, but alcohol dissolves somewhat more than its own volume of it. It can be condensed to the liquid state, at about 0° C., by the application of moderate pressure. It burns in air with a very feebly luminous flame:

$$2C_2H_6 + 7O_2 = 4CO_2 + 6H_2O$$

PROPANE, *methyl ethyl*, C_3H_8.—This gas, like methane, occurs dissolved in the Pennsylvanian petroleum springs.

BUTANES, C_4H_{10}.—As already stated, there are two isomeric butanes, *normal butane* or *diethyl*, $C_2H_5{\cdot}C_2H_5$, found in petroleum, and *isobutane* or *trimethyl methane*, $CH(CH_3)_3$ formed by artificial means.

PENTANES, C_5H_{12}.—As previously stated, three varieties are possible, and three only are known. Ordinary amyl alcohol and valerianic acid are derivatives of *isoamyl hydride* or *isopentane*.

HEXANES, C_6H_{14}.—Five are possible, five are known.

HEPTANES, C_7H_{16}.—Nine are possible, five are known.

OCTANES, C_8H_{18}.—Eighteen are possible, three are known.

NONANE, C_9H_{20}, DECANE, $C_{10}H_{22}$, and every paraffin hydrocarbon up to $C_{24}H_{50}$, as well as some others, and derivatives of much higher members of the paraffin series of hydrocarbons, are known.

General Character of the Paraffins.—The lower members of the paraffin series are gases at ordinary temperatures; the next following members, beginning with butane and isobutane, are liquids with very low boiling points, but with the boiling points rising gradually, though not quite regularly, as the number of carbon atoms in the molecule increases. When members with fifteen or more carbon atoms in their molecules are reached, these are colourless solids at ordinary temperatures, and boil at temperatures mostly above 200° C. The paraffin wax largely used in the manufacture of candles consists of a number of the higher paraffins mixed together.

The specific gravities of the liquid and solid paraffins rise gradually with the increase of molecular weight. All the paraffins are considerably lighter bulk for bulk than water. They are all very nearly insoluble in water but they are more or less soluble in alcohol and ether.

As regards their chemical characters, the paraffins are remarkable for the resistance which they offer to the action of the majority of the most active oxidizing and other agents, such as the strong acids and alkalies generally, sodium, etc. When oxidation of a paraffin takes place at all, it is frequently complete, carbonic anhydride and water being the only products formed. The paraffins are, however, easily attacked by chlorine in presence of light; less easily by bromine. These agents act by displacing one or more hydrogen atoms, and substituting chlorine or bromine for the hydrogen so displaced, hydrochloric or hydrobromic acid being formed at the same time:

$$C_nH_{2n+2} + Cl_2 = C_nH_{2n+1}Cl + HCl$$
$$C_nH_{2n+2} + Br_2 = C_nH_{2n+1}Br + HBr$$

Petroleum Spirit. Paraffin Oil. Paraffin

Petroleum Spirit, B.P. (*pentane*, C_5H_{12}, *hexane*, C_6H_{14}, etc.), known also as *benzolin*, *petroleum benzin*, and *petroleum ether* is a colourless, very volatile, and highly inflammable liquid obtained from the thin greenish *crude* petroleum, and "consisting of a mixture of the lower members of the paraffin series of hydrocarbons. Boiling-point, 122° to 140° F. (50° to 60° C.). Sp. gr. about 0·670 to 0·700." (Benzene or benzol is quite a different liquid.)

Paraffin Oil (*Paraffinum Liquidum*, B.P. and G.P., *Petrolatum Liquidum*, U.S.P.), a mixture of the higher liquid members of the paraffin series of hydrocarbons, is a clear oily liquid obtained from petroleum after distilling off the lower boiling portions. Sp. gr., 0·885 to 0·890. Boiling-point, not below 680° F. (360° C.). When heated with an equal volume of sulphuric acid, the oil is not coloured and the acid only tinged brown; when heated with metallic sodium the metal is not tarnished; alcohol boiled with the oil should not become acid. *Soft Paraffin* (*Paraffinum Molle*, B.P.), officially termed *Unguentum Paraffini* in Germany, *Pétroléine* in France, and *Petrolatum Molle* in the United States, and known in commerce by various fanciful names (vaseline, etc.), is a semi-solid mixture of paraffins, usually obtained by purifying the less volatile portions of petroleum. It is "white or yellow, translucent, soft, unctuous to the touch, free from acidity, alkalinity, or any unpleasant odour or flavour, even when warmed to 120° F. (48·9° C.). Specific gravity at the melting point 0·840 to 0·870. Melts at 96° to 102° F. (35·5° to 38·9° C.) or even somewhat higher, volatilizes without giving off acrid vapours, and burns with a bright flame, leaving no residue. Insoluble in water, slightly soluble in absolute alcohol, freely soluble in ether, chloroform, and benzol." It is not saponified by solutions of alkalies. *Hard Paraffin* (*Paraffinum Durum*, B.P.; *Petrolatum Spissum*, U.S.P.), commonly termed *paraffin wax*, or simply *paraffin*, is "a mixture of several of the harder members of the paraffin series of hydrocarbons; usually obtained by distillation from shale, separation of the liquid oils by refrigeration, and purification of the solid product. It is colourless, semi-transparent, crystalline, inodorous, and tasteless; slightly greasy to the touch. Sp. gr., 0·82 to 0·94. Insoluble in water, slightly soluble in absolute alcohol, almost entirely soluble in ether. An alcoholic solution should not redden litmus. It melts at 130° to 135° F. (54·4° to 57·2° C.), and burns with a bright flame, leaving no residue."

Paraffin resists all ordinary reagents (hence the original name *paraffin*, from *parum affinis*, without affinity), but may, by continued boiling with sulphuric acid and solution of potassium bichromate, be oxidized to *cerotic acid*, $C_{27}H_{54}O_2$. By continued digestion with nitric and sulphuric acids it yields acids of the acetic series and *paraffinic acid,* $C_{24}H_{48}O_2$ (Pouchet).

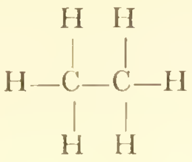
QUESTIONS AND EXERCISES

Draw graphic formulæ for methane, ethane, propane, butane, and isobutane.—How many hydrocarbons of the formula C_5H_{12} are theoretically possible and how many are known?—What is meant by *isomerism?*—Give several illustrations.—Give examples of polymeric substances.—What is meant by the term "homologous series"?—What is the general formula for the hydrocarbons of the paraffin series?—Mention some of the sources of paraffins.—Describe three general methods for the preparation of paraffins.—How would you prepare methane and ethane?—What are the substances known as petroleum spirit, paraffin oil, soft paraffin, and hard paraffin?—What is the derivation of the word paraffin?

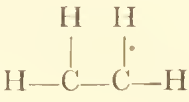
THE OLEFINE SERIES OF HYDROCARBONS

In so far as composition is concerned, any member of the olefine series differs from the paraffin which contains the same number of carbon atoms in its molecule, by containing two atoms of hydrogen fewer. The general formula for the members of the olefine series is accordingly C_nH_{2n}. This formula indicates that for each atom of carbon in the molecule of an olefine there are two atoms of hydrogen, and hence that the composition per cent. of all the olefines is the same, no matter how different their molecular weights may be. Olefines may, therefore, be looked upon as paraffins from which two atoms of hydrogen have been removed, and such evidence as is available tends to show that this is a satisfactory view of their constitution. Moreover, it would seem that the two hydrogen atoms are not to be regarded as having been removed from the same carbon atom, but from two different atoms, and that these two carbon atoms are always immediately neighbouring ones in the carbon nucleus. If this latter view is well founded, it offers some explanation for the fact that an olefine with only a single carbon atom in its molecule has never been obtained and does not appear to be capable of existence. The formula for such an olefine would be CH_2, but the lowest known member of the olefine series, *i.e.*, ethylene, is represented by the formula C_2H_4.

The paraffins have already been described as saturated compounds (p. 433). It is obvious from what has been stated in the foregoing that the olefines cannot be regarded as saturated compounds in the sense there indicated. Thus if we derive the formula for ethylene, C_2H_4, from that for ethane, C_2H_6, we should have

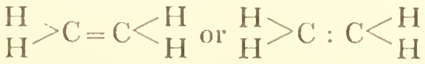
(*a*)


$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

and (*b*)


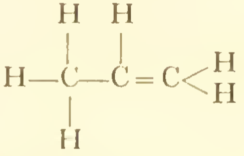
$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \end{array}$$

representing ethane and ethylene respectively. But in the formula (*b*) the combining capacity of each of the carbon atoms is represented as only three-fourths satisfied by linkage with other atoms whereas in the formula (*a*) it is represented as fully satisfied. The olefines are thus "unsaturated" compounds. It is customary in writing the formulæ for olefines, when these formulæ are extended so as to represent each carbon atom separately, to indicate the pair of carbon atoms whose combining capacity is supposed to be only three-fourths satisfied, by drawing two strokes, or, occasionally, by placing two dots between them. Thus the formula for ethylene is written



$$\begin{matrix}H\\H\end{matrix}\!>\!C=C\!<\!\begin{matrix}H\\H\end{matrix} \text{ or } \begin{matrix}H\\H\end{matrix}\!>\!C:C\!<\!\begin{matrix}H\\H\end{matrix}$$

which may be contracted into $H_2C=CH_2$ or $H_2C:CH_2$; and in the same way the formula for propylene, C_3H_6, may be written

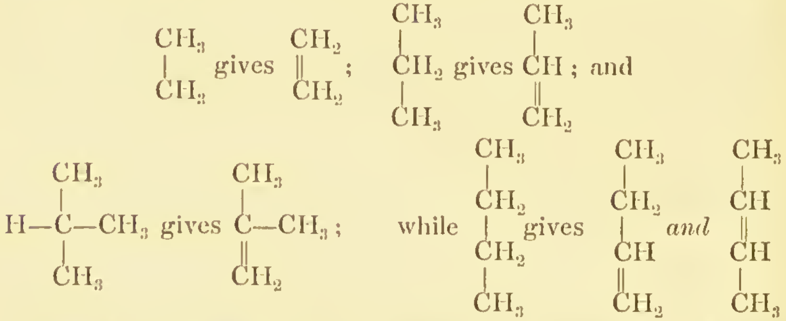


$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & = & C\!<\!\begin{matrix}H\\H\end{matrix} \\ & & | & & & & \\ & & H & & & & \end{array}$$

or $CH_3{\cdot}CH:CH_2$.

Although certain pairs of carbon atoms are represented by these formulæ as doubly linked, the assumption that these pairs of carbon atoms are *more firmly* linked to each other than in the cases where only single linkage is represented, seems not only to be unsupported but rather to be controverted by the chemical behaviour of the substances.

Isomerism in the Olefine Series.—Just as there are possible variations in the arrangement of the atoms present in those paraffins which contain four or more carbon atoms in their molecules, so in the olefines corresponding to these paraffins such variations are also possible. If the formulæ for ethane, propane, normal butane, and isobutane are considered with regard to the olefines derivable from them, it will be seen that in the cases of ethane, of propane, and of isobutane, the removal of one atom of hydrogen each from any two immediately neighbouring carbon atoms, leads to the formula of only one olefine from each paraffin, but that in the case of normal butane two different formulæ may be arrived at, depending upon which hydrogen atoms are supposed to be removed, thus:



$$\begin{array}{c}CH_3\\|\\CH_3\end{array}\text{ gives }\begin{array}{c}CH_2\\\|\\CH_2\end{array};\quad \begin{array}{c}CH_3\\|\\CH_2\\|\\CH_3\end{array}\text{ gives }\begin{array}{c}CH_3\\|\\CH\\\|\\CH_2\end{array};\text{ and}$$

$$\begin{array}{l}\;\;\;\;\;CH_3\\\;\;\;\;\;\;|\\H-C-CH_3\\\;\;\;\;\;\;|\\\;\;\;\;\;CH_3\end{array}\text{ gives }\begin{array}{l}CH_3\\|\\C-CH_3\\\|\\CH_2\end{array};\quad\text{while }\begin{array}{c}CH_3\\|\\CH_2\\|\\CH_2\\|\\CH_3\end{array}\text{ gives }\begin{array}{c}CH_3\\|\\CH_2\\|\\CH\\\|\\CH_2\end{array}\textit{ and }\begin{array}{c}CH_3\\|\\CH\\\|\\CH\\|\\CH_3\end{array}$$

There are thus three possible variations of the olefine formula C_4H_8 derivable in the manner described from the two variations (p. 434) of the paraffin formula C_4H_{10}. In agreement with this it is of interest to note that three olefines (and only three) have been obtained all with molecular weight corresponding to the formula C_4H_8. These three are commonly represented by the formulæ given above. It is here unnecessary further to discuss these olefines, or indeed any members of the series except ethylene (p. 452).

The view of the constitution of olefines in accordance with which they are regarded as paraffins from which two atoms of hydrogen have been removed (p. 448) gains support from some of the methods of general applicability by which olefines are ordinarily prepared. Of these methods, one may be discussed here with some detail, namely, that by the action of boiling alcoholic solution of potassium hydroxide upon the mono-halogen derivatives of the paraffins ($C_nH_{2n+1}X$, where X stands for Cl, Br, or I). In this interaction the potassium atom of the potassium hydroxide unites with the halogen atom of the organic halide * forming potassium halide (just as

---

* Halide is a general name sometimes employed to designate a halogen compound when it is immaterial which halogen the compound contains. (Compare p. 298.)

in the interactions of potassium hydroxide with many metallic halides) but the hydroxyl group (OH) of the potassium hydroxide does not take the place of the halogen atom (as is usual when potassium hydroxide interacts with metallic halides). Instead of this the hydroxyl group unites with a hydrogen atom of the organic halide (supposed to be a hydrogen atom linked to a carbon atom immediately adjoining the one to which the halogen atom was linked) to form water, and an olefine is produced, thus:

$$C_nH_{2n+1}X + KOH = KX + H_2O + C_nH_{2n}$$

That is to say, boiling alcoholic solution of potassium hydroxide removes hydrogen and halogen from the organic halide in the proportions in which these unite to form hydrogen halide; and the products of the action are, besides the olefine, the same substances as would be produced by the interaction of potassium hydroxide and hydrogen halide (*i.e.*, potassium halide and water).

It is of interest to note here that the mono-halogen derivatives of methane are exceptional in respect to their behaviour towards alcoholic solution of potassium hydroxide, since potassium halide and methyl alcohol are produced, by the interaction, *and no olefine*:

$$CH_3X + KOH = KX + CH_3OH$$

This exceptional behaviour is of importance as evidence in favour of the view that two different carbon atoms are concerned in the condition of non-saturation of an olefine as compared with a paraffin (p. 448). It is obvious that a molecule of methyl iodide, CH_3I, cannot lose an atom of iodine from one carbon atom and an atom of hydrogen from another.

In virtue of their character as "unsaturated" compounds the olefines combine with two halogen atoms, or with a molecule of a hydrogen halide, to form saturated compounds of the general formulæ $C_nH_{2n}X_2$ and $C_nH_{2n+1}X$ respectively.

Occurrence of Olefines in Nature.—Certain olefines occur, mixed with paraffins, in some of the natural gases and crude petroleums which issue from the earth in various parts of the world.

Production of Olefines in the Dry Distillation of Coal, etc.—Olefines are always present, and are valuable illuminating constituents, in coal gas (p. 337). The ordinary coal gas supply of towns contains from 3 to 12 per cent. by volume of olefines—chiefly ethylene.

A large number of olefines have been prepared. *Ethylene*, C_2H_4; *Propylene*, C_3H_6; *Butylene*, C_4H_8; *Amylene*, C_5H_{10}; *Hexylene*, C_6H_{12}; and *Heptylene*, C_7H_{14} are examples; and many others are well known.

Ethylene, Olefiant Gas, Heavy Carburetted Hydrogen, C_2H_4.—This olefine can be obtained by the action of boiling alcoholic solution of potassium hydroxide upon ethyl iodide (p. 459):

$$C_2H_5I + KOH = KI + H_2O + C_2H_4$$

It is usually prepared, however, from common (ethyl) alcohol, C_2H_5OH, by the action upon it, at a high temperature, of concentrated sulphuric acid.

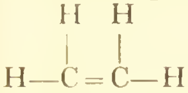
Preparation.—Ethylene may be prepared by dropping alcohol into a large retort or flask containing 10 ounces of sulphuric acid and 3 ounces of water, previously mixed, and heated to 160-165° C. The liberation of the ethylene under these conditions is supposed to be preceded by the formation of ethyl hydrogen sulphate (sulphovinic acid), $C_2H_5HSO_4$, which undergoes decomposition yielding as chief products ethylene and sulphuric acid. The gas is washed by passing it first through cold water and then through a solution of caustic soda to free it from ether, alcohol, and sulphurous anhydride.

$$\underset{\text{Alcohol}}{C_2H_5OH} + \underset{\substack{\text{Sulphuric}\\\text{acid}}}{H_2SO_4} = \underset{\substack{\text{Ethyl hydrogen}\\\text{sulphate}}}{C_2H_5HSO_4} + \underset{\text{Water}}{H_2O}$$

$$C_2H_5HSO_4 = C_2H_4 + H_2SO_4$$

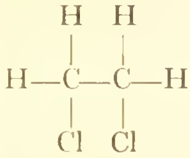
Ethylene is a colourless gas which possesses a peculiar, although not unpleasant smell. It is almost insoluble in water and is only slightly soluble in alcohol. It can be condensed to the liquid state at ordinary temperatures by the application of a pressure of about 60 atmospheres. It burns in air with a highly luminous flame, $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$. Ethylene combines directly with chlorine, with bromine, and with iodine, forming ethylene chloride, $C_2H_4Cl_2$, ethylene bromide, $C_2H_4Br_2$, and ethylene iodide, $C_2H_4I_2$ respectively. The two former are liquids (pp. 453, 454) the latter is a crystalline solid. Ethylene further unites with hydrogen bromide and with hydrogen iodide, forming ethyl bromide, C_2H_5Br, and ethyl iodide, C_2H_5I respectively.

If the graphic formula for ethylene be assumed to be

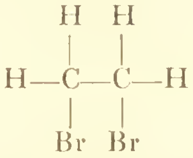


$$\begin{array}{c} H\quad H \\ |\quad\ | \\ H—C=C—H \end{array}$$

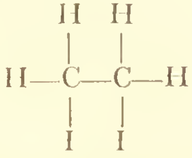
(p. 450), the formulæ for ethylene chloride, bromide, and iodide may be written as follows:—



$$\begin{array}{c} H\quad H \\ |\quad\ | \\ H—C—C—H \\ |\quad\ | \\ Cl\quad Cl \end{array}$$



$$\begin{array}{c} H\quad H \\ |\quad\ | \\ H—C—C—H \\ |\quad\ | \\ Br\quad Br \end{array}$$



$$\begin{array}{c} H\quad H \\ |\quad\ | \\ H—C—C—H \\ |\quad\ | \\ I\quad I \end{array}$$

Additional Chemical Characters of Olefines.—Besides the chemical characters of olefines already described, two others depending upon their nature as unsaturated compounds may be mentioned.

1. Olefines can be converted into paraffins by direct union with hydrogen. This is effected by passing a mixture of the olefine and hydrogen through a tube packed with platinum black.

$$C_nH_{2n} + H_2 = C_nH_{2n+2}$$

2. Olefines are absorbed by concentrated sulphuric acid (better by sulphuric acid in which sulphuric anhydride is dissolved) with the formation of compounds like ethyl hydrogen sulphate (p. 452).

$$C_nH_{2n} + \begin{matrix}H\\H\end{matrix}{>}SO_4 = \begin{matrix}C_nH_{2n+1}\\H\end{matrix}{>}SO_4$$

These compounds are of interest and importance in organic synthesis, for on heating them with water an alcohol is produced and sulphuric acid is re-formed:

$$\begin{matrix}C_nH_{2n+1}\\H\end{matrix}{>}SO_4 + H_2O = C_nH_{2n+1}OH + \begin{matrix}H\\H\end{matrix}{>}SO_4$$

Ethylene Chloride, $C_2H_4Cl_2$.—When equal volumes of ethylene and chlorine are mixed over water and exposed to daylight, they unite very readily, with the formation of oily drops which trickle down the sides of the containing vessel and collect below the water:

$$C_2H_4 + Cl_2 = C_2H_4Cl_2$$

Ethylene chloride is a colourless liquid, its odour resembling that of chloroform. It boils at 85° C.

Ethylene Bromide, $C_2H_4Br_2$.—Is prepared by bubbling ethylene into bromine (by which it is rapidly absorbed) until the colour of the bromine entirely disappears. A good deal of heat is given out during the combination, and the bromine must be kept cold:

$$C_2H_4 + Br_2 = C_2H_4Br_2$$

Ethylene bromide is a colourless liquid possessing a pleasant ethereal smell. It boils at 133°C.

THE ACETYLENE SERIES OF HYDROCARBONS

Each member of this series of hydrocarbons differs from the paraffin with the same number of carbon atoms in its molecule, by containing four atoms of hydrogen fewer. The general formula for the acetylene series is therefore C_nH_{2n-2}.

The first member of this series is acetylene, C_2H_2. Other members are *Allylene,* C_3H_4; *Crotonylene,* C_4H_6; etc. Acetylene is the only one which will be treated of here. The following discussion of one of the modes of formation of acetylene should give a sufficient view of the way in which this hydrocarbon is supposed to be constituted. The change which takes place when the mono-halogen derivatives of the paraffins ($C_nH_{2n+1}X$) are acted upon by a boiling alcoholic solution of potassium hydroxide has already been stated on p. 451 as resulting in the removal, from each molecule, of the halogen atom and a hydrogen atom. When a di-halogen derivative of a paraffin ($C_nH_{2n}X_2$) is subjected to the same action an exactly analogous change usually takes place, but in such a case each molecule often loses *both* halogen atoms and *two* hydrogen atoms. Thus when ethylene bromide, $C_2H_4Br_2$ (*see* above) is employed, acetylene is produced:

$$C_2H_4Br_2 + 2KOH = 2KBr + 2H_2O + C_2H_2$$

The action in this case can be separated in actual experiment into two stages: in the first, one halogen atom and one hydrogen atom are removed; in the second the remaining halogen atom and another hydrogen atom are removed.

Acetylene, C_2H_2.—This hydrocarbon is produced by direct union of the elements when electric sparks are passed between carbon terminals in an atmosphere of hydrogen. This method of production is of great interest as a mode of obtaining an organic compound from purely inorganic materials. Acetylene is also produced in small quantity in many cases of incomplete combustion of substances containing carbon and hydrogen. One of the best known instances of this is its formation in a Bunsen burner when the gas is kindled at the gas inlet jet (close beside the air inlet holes at the base of the upright metal tube). Formerly when acetylene was required in quantity it was obtained either from this source by separating it from the other products of the combustion, or else by the action of boiling alcoholic solution of potassium hydroxide on ethylene bromide as already discussed in the preceding paragraph. It is now prepared as a commercial product on the large scale for illuminating purposes, by the action of water upon calcium carbide, CaC_2 :

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

The solid carbide is simply treated with cold water, when a brisk effervescence at once takes place.

Acetylene is a colourless gas possessing a disagreeable odour. It burns in air with an intensely luminous flame :

$$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O$$

A mixture of acetylene and oxygen in the proportions represented by the above equation, explodes with extreme violence on the application of a light.

A striking property of acetylene (and one characteristic of hydrocarbons in which the group $—C : C—H$ is assumed to exist) is that of combining to form compounds containing copper or silver, and commonly called "acetylides." Thus when acetylene is bubbled into an ammoniacal solution of cuprous chloride a reddish-brown precipitate is produced of copper acetylide, the composition of which is generally supposed to be represented by the formula $C_2H_2Cu_2O$. This copper compound is usually preserved in a moist condition, because when dry it is liable to explosive decomposition by friction or by gentle heating. It may be decomposed by the action of concentrated hydrochloric acid, or better of potassium cyanide solution, when acetylene is liberated.

In accordance with its character as an unsaturated compound, acetylene combines directly with hydrogen to form ethylene, which in turn combines with hydrogen to form ethane (compare p. 453). Acetylene also combines directly with the halogens and with hydrogen halides, fully saturated compounds, such as $C_2H_2Br_4$, etc., being obtained as final products.

A highly important character of acetylene is its convertibility into benzene. The conversion is slowly effected by exposing it for some time to a high temperature, $3C_2H_2 = C_6H_6$. This change is a good example of polymerisation, and further, it furnishes an example of the formation of an "aromatic" compound from a "fatty" one.

Other Series of Hydrocarbons.—There are other series of fatty hydrocarbons whose members contain hydrogen in still smaller proportion relatively to the carbon than is the case with the members of the paraffin, the olefine, and the acetylene series; but these cannot be treated of here.

QUESTIONS AND EXERCISES

What is the general formula for the hydrocarbons of the olefine series?—How many olefines of the formula C_4H_8 are known?—How is ethylene prepared and what are its properties?—How may ethylene chloride and bromide be prepared?—What is the general formula for the hydrocarbons of the acetylene series?—How is acetylene prepared and what are its chief properties?—How may benzene be prepared from acetylene?

Halogen Derivatives of the Paraffins

The members of the paraffin series of hydrocarbons have already been discussed as saturated compounds, and as such they do not unite with the halogens to form halogen-addition products, *i.e.*, products containing all the atoms of the original paraffins, and halogen atoms besides. But compounds can be obtained which may be looked upon as paraffins in whose molecules the place of a part or of the whole of the hydrogen is taken by halogen. Such compounds, of which several have been mentioned already, are commonly called halogen derivatives of the paraffins. It is only necessary to mention here some of the commoner methods for the preparation of these derivatives, and to discuss some of the substances themselves which are of the greatest theoretical interest or practical importance.

1. The hydrogen of the paraffins (or in some cases a part of it at least) can be displaced and chlorine "substituted" for it by treating the paraffins with chlorine in daylight. This is called "chlorination" or "chlorine-substitution." Bromine, under the same conditions, behaves similarly but somewhat less readily unless the action is assisted by heating. Iodine, on the other hand, scarcely acts in this way at all. In the case of methane the hydrogen is removed and chlorine substituted for it in stages, with the formation of four different products, as represented by the four following equations:

$$CH_4 + Cl_2 = HCl + CH_3Cl \qquad CH_2Cl_2 + Cl_2 = HCl + CHCl_3$$
$$CH_3Cl + Cl_2 = HCl + CH_2Cl_2 \qquad CHCl_3 + Cl_2 = HCl + CCl_4$$

The products (other than the hydrochloric acid) of these four reactions are named as under:

CH_3Cl	Mono-chloro-methane; or methyl chloride.
CH_2Cl_2	Di-chloro-methane; or methylene chloride.
$CHCl_3$	Tri-chloro-methane; or methenyl or formyl chloride; or chloroform.
CCl_4	Tetra-chloro or perchloro-methane or carbon tetrachloride.

Starting from methane, however, more than one of the above four reactions take place to some extent side by side no matter how small the proportion is in which the chlorine is employed; so that this is not a suitable method for obtaining pure intermediate products.

2. Halogen derivatives of the paraffins are produced when hydrocarbons of the ethylene and acetylene series combine with halogens or with hydrogen halides to form saturated compounds. Thus ethylene and acetylene combine with bromine and with hydrobromic acid to form saturated compounds.

3. Mono-halogen derivatives of the paraffins are prepared by the action of the hydrogen halides, or better, of the phosphorus halides upon alcohols of the general formula $C_nH_{2n+1}OH$; water, or an oxygenated compound of phosphorus (phosphorous or phosphoric acid, or a phosphorus oxyhalide) being formed at the same time:

$$C_nH_{2n+1}OH + HX = H_2O + C_nH_{2n+1}X$$
$$3C_nH_{2n+1}OH + PX_3 = H_3PO_3 + 3C_nH_{2n+1}X$$

When the hydrogen halides are employed the reactions never become complete, but a balance is eventually established owing to the tendency of the water formed to interact with the halogen derivative, and produce alcohol and acid again. When the phosphorus halides are employed other reactions besides that represented by the above equation take place to a considerable extent.

Methyl and ethyl iodides are usually prepared by the action of phosphorus tri-iodide upon methyl and ethyl alcohols respectively:

$$3CH_3OH + PI_3 = H_3PO_3 + 3CH_3I$$
$$3C_2H_5OH + PI_3 = H_3PO_3 + 3C_2H_5I$$

It is not necessary that the phosphorus tri-iodide should be prepared beforehand and then added to the alcohol. It is sufficient to mix the alcohol with phosphorus and then to add the iodine slowly. Red phosphorus is generally employed. The course of the reaction may fairly be assumed to consist in the formation, in the first place, of phosphorus tri-iodide, which then interacts with the alcohol as represented above. The methyl or ethyl iodide is distilled away from the phosphorous acid and other products of the reaction, and is further purified by drying over calcium chloride and subsequent redistillation.

Methyl Chloride, CH_3Cl, and *Methyl Bromide*, CH_3Br, are gases at ordinary temperatures, but both can easily be condensed to the liquid state. The former is prepared from one of the by-products of the beet-sugar manufacture, and has found several industrial applications.

Ethyl Chloride, C_2H_5Cl, and *Ethyl Bromide*, C_2H_5Br, are liquids with low boiling points. The latter has been employed as an anæsthetic in dentistry. It may be prepared by gradually adding 6 parts of bromine to a mixture of 6 parts of ethyl alcohol and 1 of amorphous phosphorus contained in a flask fitted with an upright condenser, care being taken to keep the apparatus cool:

$$3C_2H_5OH + PBr_3 = 3C_2H_5Br + H_3PO_3$$

When all the bromine has been added, the mixture is poured into a retort and distilled over a water-bath, the resulting ethyl bromide freed from excess of bromine by washing with a small quantity of dilute caustic soda or potash, then washed with water, dried over calcium chloride, and redistilled.

For the preparation of ethyl bromide on a large scale, De Vrij's method is preferable, $C_2H_5HSO_4 + KBr = C_2H_5Br + KHSO_4$ (*see Pharm. Journ.*, 15th Feb. 1879), or the same method as modified by Greene (*P. J.*, 12th July 1879), by Remington (*P. J.*, 29th May 1880), or by Wolff (*P. J.*, 3rd July 1880).

Methyl and *Ethyl Iodides*, CH_3I and C_2H_5I, are generally prepared by the method already described (method 3 *ante*). They are both colourless liquids of peculiar but not unpleasant smell. Methyl iodide boils at 45° C.; ethyl iodide at 72·3° C. Both iodides are very largely employed, and are of great importance, in the synthetic formation of other organic compounds. Instances of their employment have already been given on pp. 440, 441, etc. They should be kept in the dark, as exposure to light promotes decomposition with separation of iodine.

Chloroform

Chloroform or Trichloromethane (*Chloroformum*, B.P.), $CHCl_3$. This very important substance is prepared in large quantity for use as an anæsthetic, as a solvent, and for other purposes. It is prepared on the commercial scale, in metal stills, by the action of bleaching-powder, at a temperature of about 45° C., on ordinary alcohol which has been diluted with about 16 to 20 times its weight of water. When the reaction has set in no further heating is necessary, as sufficient heat is given out during its progress. A mixture of substances distils off, and, on being condensed to the liquid state the distillate separates into two layers. The lower layer, which consists of crude chloroform, is separated from the upper aqueous layer, and is purified by shaking it with water and then with pure sulphuric acid (containing no trace of nitric acid), which chars and removes hydrocarbons, etc., but does not affect chloroform. It is freed from any trace of acid by agitation with lime, and from moisture by solid calcium chloride. It is finally rectified. Instead of alcohol, commercial acetone is now largely employed as a substitute in the preparation of chloroform, the product being known in trade as "*ketone chloroform*." The exact nature of the changes which take place in the preparation of chloroform from alcohol or acetone is not only complicated but also somewhat obscure.

Experiment.—Place $1\frac{1}{2}$ fluid ounce of alcohol (90 per cent.) and 24 ounces of water in a retort or flask of at least a quart capacity; add 8 ounces of chlorinated lime and 4 of slaked lime; connect the vessel with a condenser, and heat the mixture until distillation commences, the source of heat then being withdrawn. The condensed liquid should fall into a small flask containing water, at the bottom of which about a drachm of chloroform will slowly collect.

Chloroform is produced when chloral is warmed with aqueous solution of potassium or of sodium hydroxide, and for the sake of greater purity it is sometimes prepared from chloral in this way. It is stated that chloroform is also manufactured by the action of chlorine upon methyl chloride (compare p. 457).

Properties.—The sp. gr. of pure chloroform is at least 1·500, perhaps higher. It is liable to slowly decompose when exposed to air and light; $4CHCl_3 + 3O_2 = 4COCl_2 + 2H_2O + 2Cl_2$. The resulting chlorine may be detected by adding zinc iodide and starch, and the carbon oxychloride (carbonyl chloride, phosgen, p. 340) by means of baryta water: $COCl_2 + 2Ba(OH)_2 = BaCO_3 + BaCl_2 + 2H_2O$. To render chloroform stable, a minute amount (1 volume in 100 or less) of absolute alcohol is necessary: hence the specific gravity of medicinal chloroform is about 1·490 to 1·495. Chloroform is not decomposed by the action of sunlight unless oxygen is present, when, in the first stages of the decomposition, chlorine is liberated, and this, acting on the alcohol contained in the chloroform, produces hydrogen chloride, which is then found instead of free chlorine. Hence the liberation of chlorine has been disputed by some who have overlooked the presence of alcohol in the chloroform operated on. Chloroform readily and entirely volatilizes at ordinary temperatures, having, to the last drop, its pleasant characteristic odour. It has a sweetish taste, is limpid, colourless, miscible in all proportions with alcohol and ether, and slightly soluble in water. It may be so frozen at low temperatures that any impurities shall remain in the still fluid portion (Pictet). It boils between

140° and 143·6° F. (60° and 62° C.). It burns with a sluggish, green, smoky flame. It reduces Fehling's solution. It should be neutral to test-paper, indicating absence of acid; give no precipitate with solution of silver nitrate, indicating absence of ordinary chlorides; remain colourless when heated with caustic potash, indicating absence of aldehyde; and when shaken with concentrated sulphuric acid should give no more colour than is producible by the absolute alcohol that is present, even after the mixture has been set aside for half an hour, indicating absence of hydrocarbons, etc. Alcohol may be detected by the iodoform test, or by shaking with a little of the dye termed "Hofmann's violet," which gives the chloroform a purple tint if alcohol be present, but affords no colour with pure chloroform. At the temperature of melting ice, chloroform unites with water to form a crystalline compound, $CHCl_3, 18H_2O$.

Chloroform is an important solvent; it dissolves sulphur, phosphorus, and iodine, as well as fats, resins, indiarubber, alkaloids, many alkaloidal salts, and numerous other organic compounds.

Chromic anhydride acts on chloroform, converting it into phosgen, $COCl_2$.

Aqua Chloroformi, B.P., the official Chloroform Water, is made by shaking 30 minims of chloroform with 25 ounces of distilled water till dissolved.

Iodoform

Iodoform or *Tri-iodomethane* (*Iodoformum*, B.P. and U.S.P.), CHI_3, is analogous in constitution to chloroform, the iodine occupying the place of the chlorine. It is made by mixing together one part of alcohol, two parts of crystallized sodium carbonate, and ten parts of water; the whole being heated to about 150° F. (65·6° C.), and one part of iodine gradually added in small portions. When the liquid becomes colourless, the iodoform is allowed to settle. It is then collected on a paper filter, washed thoroughly with water, and dried between filter-paper. (This reaction forms a very delicate means of testing for the presence of alcohol.)

Iodoform is now prepared on the manufacturing scale by the electrolysis of a solution in aqueous alcohol of potassium iodide and potassium carbonate, carbonic anhydride being passed into the solution from time to time to convert into carbonate the potassium hydroxide formed during the electrolysis. Chloroform and *bromoform* may be obtained in an analogous manner, potassium chloride or bromide being substituted for the potassium iodide.

Iodoform occurs as yellow, shining, six-sided scales. It is volatile at ordinary temperatures; almost insoluble in water, soluble in alcohol or ether. Warmed with an alcoholic solution of caustic potash, potassium formate and iodide are produced, $CHI_3 + 4KOH = HCOOK + 3KI + 2H_2O$; and the resulting fluid, heated with a little nitric acid, yields free iodine, recognisable by its colour or by giving a blue reaction with starch.

Esters

The paraffins give rise to many substitution derivatives by displacement of their hydrogen by compound acid radicals. These derivatives are now commonly designated by the German word "ester."* The following, chiefly derived from ethane and pentane, are of pharmaceutical interest:—

Spirit of Nitrous Ether

Ethyl Nitrite, Nitrous Ether, $C_2H_5NO_2$.—A "spirit," probably containing nitrous ether, was one of the earliest known medicinal compounds, its discovery being generally ascribed to Raymond Lully.

Experiment.—To a third of a test-tubeful of alcohol (90 per cent.) add about a tenth of its bulk of sulphuric acid, rather more of nitric acid, and some copper wire or turnings, and warm the mixture; as soon as ebullition commences, the vapour of nitrous ether (with other substances) is evolved, recognisable by its odour. A long bent tube, kept very cool to serve as a condenser, may be adapted by means of a perforated cork to the test-tube, and thus a little of the product may be condensed and collected.

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* The name ester is now used instead of "compound ether" or "ethereal salt" terms which were formerly in general use. The use of the word ether in strictly systematic chemical nomenclature, is now confined to a different group of organic compounds (*see* p. 519), but in popular language, and in pharmacy, the word is not always confined to this group.

The above process conducted on a larger scale, with definite quantities of materials, temperature regulated by a thermometer, and a well-cooled condenser, etc. (*see* p. 139), is the official process (Kopp's process applied by Redwood) for the preparation of a concentrated solution of nitrous ether, etc., in alcohol; diluted with more alcohol (90 per cent.), the product forms the official spirit of nitrous ether (*Spiritus Ætheris Nitrosi*, B.P.) of pharmacy.

Disregarding the other products formed besides ethyl nitrite and aldehyde, the following equation probably represents the chief decompositions that occur in the operation. An important feature in the reaction is the reduction of the nitric to the nitrous radical :—

$$\underset{\text{Alcohol}}{3C_2H_5OH} + \underset{\substack{\text{Nitric}\\\text{acid}}}{2HNO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid}}}{H_2SO_4} + \underset{\text{Copper}}{Cu}$$

$$= \underset{\substack{\text{Nitrous}\\\text{ether}}}{2C_2H_5NO_2} + \underset{\text{Aldehyde}}{C_2H_4O} + \underset{\text{Water}}{4H_2O} + \underset{\substack{\text{Cupric}\\\text{sulphate}}}{CuSO_4}$$

Properties.—Spirit of Nitrous Ether is "a limpid liquid having a very faint yellowish tinge, inflammable, of a peculiar penetrating apple-like odour, and a characteristic taste. Sp. gr., 0·838 to 0·842. It should not effervesce, or only very feebly, when shaken with sodium bicarbonate" (showing absence of appreciable quantities of free nitrous, acetic or other acids). The aldehyde in it may be detected by the caustic potash test (*see* "Aldehyde, Test for" in Index). The great tendency of aldehyde to become converted into acetic acid by the absorption of oxygen from the air renders Spirit of Nitrous Ether unstable, and pharmacists are obliged to neutralize such acid, generally by means of potassium bicarbonate, before adding it to medicines containing iodides, etc. The nitrous radical may be detected by adding a concentrated solution of ferrous sulphate mixed with sulphuric acid to some of the spirit of nitrous ether, the usual dark compound being produced.

Official (B.P.) *test of strength.*—1 volume agitated briskly at intervals during five minutes in a brine-charged nitrometer, with 1 volume of solution of potassium iodide and 1 volume of diluted sulphuric acid, should yield, at the normal temperature (60° F. or 15·5° C.) and pressure (30 inches or 760 millimetres of mercury), and when freshly prepared, at least $6\frac{1}{4}$, but not more than 7, volumes of nitric oxide gas, corresponding to at least $2\frac{1}{2}$ parts by weight of ethyl nitrite in 100 parts by weight of the Spirit: and even after it has been kept for some time, and the vessel containing it has occasionally been opened, it should yield not much less than 5 times its volume of the gas, corresponding to nearly 2 per cent. by weight of ethyl nitrite or a minimum of $1\frac{3}{4}$ per cent.

The reaction which takes place in the foregoing test is as follows:—

$$2C_2H_5NO_2 + 2KI + 2H_2SO_4 = 2C_2H_5OH + 2KHSO_4 + I_2 + 2NO.$$

For the detection of methyl alcohol in spirit of nitrous ether, *see* "Methylated Sweet Spirit of Nitre," p. 484.

A very old variety of spirit of nitrous ether, or rather of "sweet spirit of nitre" (*Spiritus Nitri Dulcis.* P. L., 1746), still sold in Great Britain, is made from rectified spirit and nitric acid, as ordered in the London Pharmacopœias, except that the distillation is continued until the product has a sp. gr. of 0·850. It may contain little or no ethyl nitrite, but is popular as a stimulant. By "Sweet Spirit of Nitre" the official Spirit of Nitrous Ether is now (B.P., 1898) to be understood unless some other variety is indicated.

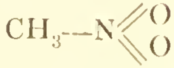
Pure Ethyl Nitrite.—Dr Leech states that the physiological and the therapeutic action of "spirit of nitrous ether" is similar to that of an alcoholic solution of ethyl nitrite of similar nitrous strength. The nitrite was prepared for Dr Leech in the Research Laboratory of the Pharmaceutical Society of Great Britain, by Hare's process of mixing sodium nitrite, sulphuric acid, and alcohol at a low temperature—but, perhaps, for the first time, in a pure condition. The nitrite separates as a pale yellow layer. It may be washed rapidly with a little water and dehydrated with dry potassium carbonate. As ethyl nitrite is decomposed by prolonged contact with water, Dr Leech was supplied, according to suggestions and experiments by the late John Williams, with a pure solution of it in absolute alcohol containing 5 per cent. of glycerin as a preservative.

$$\underset{\substack{\text{Sodium}\\\text{nitrate}}}{2NaNO_2} + \underset{\substack{\text{Sulphuric}\\\text{acid}}}{H_2SO_4} + \underset{\text{Alcohol}}{2C_2H_5OH} = \underset{\substack{\text{Ethyl}\\\text{nitrite}}}{2C_2H_5NO_2} + \underset{\substack{\text{Sodium}\\\text{sulphate}}}{Na_2SO_4} + \underset{\text{Water}}{2H_2O}$$

Liquor Ethyl Nitritis, B.P., is made as above. It should contain, when fresh, 3 per cent., and even when long kept not less than 2½ per cent., by weight, of ethyl nitrite. Sp. gr., 0·823 to 8·826. It should yield 7·6 times its volume of nitric oxide, or at least five-sixths of that quantity. It should be dispensed and used from small bottles to avoid loss by volatilization and to prevent absorption of moisture from the air.

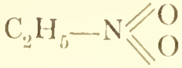
Nitro-compounds.—There are two derivatives of ethane which possess the composition represented by the formula $C_2H_5NO_2$ but which differ very much in properties, namely, *ethyl nitrite*, which boils at 63·5° F. (17·5° C.) and has a sp. gr. of 0·900 (at 0° C.; water = 1; 0·917 to 0·920; Dunstan and Dymond) and *nitro-ethane* which boils at about 235° F. (nearly 113° C.) and has a sp. gr. of 1·058. The official spirit of nitrous ether contains ethyl nitrite. There are also two analogous derivatives of methane (CH_3NO_2), namely, methyl nitrite and nitro-methane. The nitrites are easily decomposed, the nitro-compounds are stable. Moreover, the reactions of the two sets of compounds warrant the conclusion that in the nitrites the methyl or ethyl group is united to oxygen, in the nitro-compounds to the nitrogen. The nitrites are, the nitro-compounds are not, saponifiable; on reduction, the nitrogen of the former does not, while that of the latter does, remain with the radicals, yielding amines. Possibly the nitrites contain the nitrogen in the trivalent condition, while in the nitro-compounds it is quinquivalent, as represented by the following formulæ for the compounds just mentioned as well as for the two corresponding derivatives of pentane, namely, amyl nitrite and nitro-pentane:—

Methyl nitrite, $CH_3—O—N=O$. Nitro-methane,



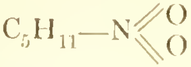
$$CH_3—N\begin{array}{l}\diagup\!\!\!\diagup O\\ \diagdown\!\!\!\diagdown O\end{array}$$

Ethyl nitrite, $C_2H_5—O—N=O$. Nitro-ethane,



$$C_2H_5—N\begin{array}{l}\diagup\!\!\!\diagup O\\ \diagdown\!\!\!\diagdown O\end{array}$$

Amyl nitrite, $C_5H_{11}—O—N=O$. Nitro-pentane,



$$C_5H_{11}—N\begin{array}{l}\diagup\!\!\!\diagup O\\ \diagdown\!\!\!\diagdown O\end{array}$$

Ethyl Acetate or Acetic Ether

Ethyl Acetate or *Acetic Ether* (*Æther Aceticus*, B.P.), $CH_3·CO·OC_2H_5$, or $C_2H_5C_2H_3O_2$.—To a little dried sodium acetate, in a test-tube, add a small quantity of alcohol and some sulphuric acid. Adapting a long bent tube in the usual manner, heat the test-tube and so distil over acetic ether—which may be collected in another test-tube kept cool by partial immersion in cold water.

On a larger scale the following proportions may be used: alcohol (90 per cent.) $32\frac{1}{4}$ fluid parts; sulphuric acid, $32\frac{1}{2}$ fluid parts; sodium acetate, 40 parts; potassium carbonate, freshly dried, 6 parts. Slowly add the acid to the alcohol, keeping the liquid cool, and the product being cold, add the acetate, mixing thoroughly. Distil forty-five fluid parts. Digest the distillate with the potassium carbonate for three days in a stoppered bottle. Separate the ethereal fluid, and again distil until all but about four fluid parts have passed over. Preserve the resulting acetic ether in a well-closed bottle and in a cool place. It is a colourless liquid with an agreeable ethereal odour. Sp. gr., 0·900 to 0·905. Boiling-point, about 166° F. (74·4° C.). Soluble in all proportions in alcohol (90 per cent.) and in ether. One part, by weight, dissolves in about 10 parts of water at 60° F. (15·5° C.).

$$\underset{\text{Alcohol}}{C_2H_5OH} + \underset{\substack{\text{Sodium}\\\text{acetate}}}{CH_3{\cdot}CO{\cdot}ONa} + \underset{\substack{\text{Hydrogen}\\\text{sulphate}}}{H_2SO_4}$$

$$= \underset{\substack{\text{Ethyl}\\\text{acetate}}}{CH_3CO{\cdot}OC_2H_5} + \underset{\substack{\text{Sodium hydro-}\\\text{gen sulphate}}}{NaHSO_4} + \underset{\text{Water}}{H_2O}$$

Ethyl aceto-acetate, or aceto-acetic ether, is of great importance in synthetic chemistry, as through its means a variety of substances can be built up. In constitution it is the ethyl salt of aceto-acetic acid, and its formula is $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5$. It is prepared by acting on ethyl acetate with sodium, treating the product with a dilute acid, and subjecting the crude aceto-acetic ether to fractional distillation.

Amyl Acetate, $CH_3{\cdot}CO{\cdot}OC_5H_{11}$, or $C_5H_{11}C_2H_3O_2$.—To a small quantity of amyl alcohol (fusel oil may be used) in a test-tube add some potassium acetate and a few drops of sulphuric acid, and warm the mixture; the vapour of amyl acetate is evolved, recognisable by its odour, which resembles that of the jargonelle pear. If a condensing tube be attached, the acetate may be distilled over, washed by agitation with water, to free it from alcohol, and separated by means of a pipette.

$$\underset{\text{Potassium acetate}}{CH_3{\cdot}CO{\cdot}OK} + \underset{\text{Amyl alcohol}}{C_5H_{11}OH} + \underset{\text{Sulphuric acid}}{H_2SO_4}$$

$$= \underset{\text{Amyl acetate}}{CH_3{\cdot}CO{\cdot}OC_5H_{11}} + \underset{\text{Acid potassium sulphate}}{KHSO_4} + \underset{\text{Water}}{H_2O}$$

Artificial fruit-essences.—Amyl acetate, prepared with the proper proportions of materials, as indicated by the above equation, is largely manufactured for use as a flavouring agent by confectioners. Amyl valerianate, $C_5H_{11}C_5H_9O_2$, is similarly used under the name of apple-oil. Ethyl butyrate, $C_2H_5C_4H_7O_2$, closely resembles the odour and flavour of pineapple; ethyl œnanthylate, $C_2H_5C_7H_{13}O_2$, recalls green-gage; ethyl pelargonate, $C_2H_5C_9H_{17}O_2$, quince; ethyl suberate, $(C_2H_5)_2C_8H_{12}O_4$, mulberry; ethyl sebacate, $(C_2H_5)_2C_{10}H_{16}O_4$, melon. By mixing such esters with each other and with essential oils in various proportions, the odour and flavour of nearly every fruit may be imitated.

Amyl Nitrite

Amyl Nitrite, $C_5H_{11}NO_2$ (*Amyl Nitris*, B.P.).—This may be prepared by the direct action of nitric acid on amyl alcohol, the nitric acid being reduced to nitrous by a portion of the alcohol, valerianic aldehyde and valerianic acid also being produced. The temperature must be very carefully regulated, or the reaction may become extremely violent; indeed, even with small quantities a violent explosion may occur. For experimental purposes it is preferable to pass the nitrous gases generated by the action of nitric acid on white arsenic or on starch, into the amyl alcohol (kept cool by placing the vessel in cold water) until the alcohol is saturated. The product is shaken with an aqueous solution of potassium hydroxide or carbonate to remove free acids, and the oily liquid is then separated and distilled. The portion distilling between 205° and 212° F. (96° to 100° C.) is amyl nitrite.

The official amyl nitrite is a yellowish ethereal liquid; sp. gr., 0·870 to 0·880; boiling-point, 205° F. (96° C.); soluble in alcohol, insoluble in water; converted by fused caustic potash into potassium valerianate; exposed to the air, it yields amyl alcohol. If of good quality (for physiological purposes, although perhaps not chemically pure), about 70 per cent. will distil between 194° and 212° F. (90° to 100° C.), the bulb of the thermometer being in the vapour and not touching the residual fluid.

The official and commercial varieties of "amyl nitrite" are well known to be only "chiefly" (B.P.) real amyl nitrite. The staff of the Research Laboratory of the Pharmaceutical Society have shown that the fluid may contain both alpha-amyl and beta-amyl nitrites, iso-butyl nitrite, and propyl nitrite. These nitrites are, of course, derived from the corresponding alcohols (*see* p. 492) present in the crude amyl alcohol of commerce.

Nitropentane, $C_5H_{11}NO_2$, is similar to amyl nitrite in composition, but differs much in properties. It is obtained by the interaction of amyl iodide and silver nitrite. It boils at 300° to 320° F. (148·8° to 160° C.).

QUESTIONS AND EXERCISES

Give details of the production of chloroform from alcohol.—Give two ways of preparing iodoform.—Give the formulæ and state the constitution of the various chlorine derivatives of methane.—How is chloroform purified?—State the characters of pure chloroform.—Explain the official process for the preparation of nitrous ether.—Give the properties of nitrous ether as compared with nitro-ethane.—By what official method is the strength of spirit of nitrous ether to be estimated?—How is ethyl iodide made?—Mention the systematic names of several artificial fruit-essences.—What is the formula of amyl nitrite, and how is it prepared?

THE BENZENE SERIES OF HYDROCARBONS

The Benzene or *Aromatic Series*, C_nH_{2n-6}.—This series is of great general interest. Just as each consecutive member of the paraffin series of hydrocarbons may be regarded as derived by the displacement of a hydrogen atom of the preceding member by the methyl (CH_3) group, or of a hydrogen atom in methane by a paraffin radical, so the consecutive members of the benzene series of hydrocarbons may for convenience of study be viewed as obtained by the displacement of one or more hydrogen atoms in *benzene* by paraffin radicals; as in the following examples:—

Benzene, C_6H_6.
Toluene or Methylbenzene, C_7H_8 or $C_6H_5 \cdot CH_3$.
Xylene or Dimethylbenzene, C_8H_{10} or $C_6H_4 \cdot (CH_3)_2$.
Mesitylene or Trimethylbenzene, C_9H_{12} or $C_6H_3 (CH_3)_3$.
Cymene or Methyl-isopropylbenzene, $C_{10}H_{14}$ or $C_6H_4 \cdot CH_3 \cdot C_3H_7$.

The members of the benzene series are *unsaturated* hydrocarbons. A molecule of benzene itself readily unites with two, four, or six atoms of chlorine, forming what are termed addition compounds, as distinguished from the substitution compounds, in which the hydrogen atoms in benzene are actually substituted by chlorine, bromine, etc. The derivatives of benzene may more or less readily be re-converted into benzene, a fact supporting the close structural or constitutional relationship existing amongst them.

A number of well-known substances possessing aromatic odours were amongst the earliest known derivatives of the benzene series of hydrocarbons, hence the benzene series was originally termed the *aromatic series* of organic compounds.

Benzene or Benzol

Benzene, C_6H_6 (commonly known as *Benzol*) *, is obtained commercially from the portion of coal tar boiling below 100° C. This distillate is partially purified by shaking successively with sulphuric acid, water, and caustic soda, and then redistilling; the product still contains large quantities of toluene and other impurities. If pure benzene is required, the liquid must be cooled by means of a freezing mixture, when the benzene crystallizes out, leaving some impurities in solution; the crystals are well drained. Bromine is then added to the liquid resulting from the melting of the crystals, until a permanent coloration results. The liquid is again washed with caustic soda, and distilled. Benzene boils at 81° C. It is a colourless, limpid, highly refractive liquid, of sp. gr., 0·899 at 0° C. It is a valuable solvent of fats and oils, and under the name of "Benzine Collas" was introduced by M. Collas in 1848 for cleansing purposes.

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* *Note.*—The student must avoid confusing coal-tar *benzene*, C_6H_6, with petroleum *benzin*, petroleum ether, benzolin, etc., (*Petroleum Spirit*, B.P.), which are mixtures of paraffin hydrocarbons of lower boiling-points.

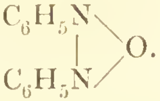
Benzin (U.S.P.), C_5H_{12}, C_6H_{14}, and other hydrocarbons of the paraffin series (of boiling-point 122-140° F.), require six times their volume of alcohol for solution, whereas *benzene*, C_6H_6, dissolves in less than its own volume. Specific gravity of *benzene* about 0·850; of *benzin* about 0·700.

Benzene may be obtained from benzoic acid by heating with lime. It is also formed on passing acetylene through red-hot tubes.

When acted on by chlorine and by bromine, in the presence of a little iodine, benzene yields all derivatives from monochloro- and monobromo-benzene (C_6H_5Cl and C_6H_5Br) to hexachloro- and hexabromo-benzene (C_6Cl_6 and C_6Br_6). Benzene also forms iodine and fluorine derivatives, nitro-derivatives, etc.

Benzol, B.P., "a mixture of homologous hydrocarbons obtained from light coal-tar oil," contains about 70 per cent. of benzene.

Nitrobenzene (nitrobenzol, artificial oil of bitter almonds, or essence of mirbane), $C_6H_5NO_2$, is obtained by slowly mixing fuming nitric acid, or a mixture of nitric and sulphuric acids, with benzene, the vessel being kept cool by immersion in water. It is a yellow liquid, heavier than water, having a strong odour resembling that of oil of bitter almonds. When acted on by a powerful reducing mixture such as iron and acetic acid, or tin and hydrochloric acid (yielding nascent hydrogen), it is converted into aniline.

Aniline or *Phenylamine*, $C_6H_5NH_2$.*—Mix 13 parts of iron filings, 7 or 8 of ordinary acetic acid, and 13 of nitrobenzene, in a large flask (with an upright condenser) placed on a water-bath, and, after the mixture has digested for several hours, pour off the supernatant liquid from the deposit of iron filings, and distil in a current of steam. By this method the nitrobenzene yields, first, aniline, distilled over as a yellow oil, and afterwards a red oil, which is a mixture of azobenzene, $C_6H_5{\cdot}N=N{\cdot}C_6H_5$, hydrazobenzene, $C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_6H_5$, and azoxybenzene,  $\left.\begin{matrix} C_6H_5N \\ | \\ C_6H_5N \end{matrix}\right\rangle O$.

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* Aniline may be obtained from indigo, hence its name, *anil* being Portuguese for indigo.

Aniline, $C_6H_5NH_2$ (mixed with toluidine, $C_7H_7NH_2$), when oxidized by arsenic acid, or chlorinated lime, produces *rosaniline*, $C_{20}H_{19}N_3$, whose salts and derivatives form a number of the well-known aniline colours.

Constitution of Amines.—Amines are usually regarded as derivatives of ammonia, one, two, or three atoms of hydrogen being replaced by one, two, or three univalent organic radicals, or equivalents of radicals of higher quantivalence. The products are called primary, secondary, and tertiary amines. The class includes certain alkaloids.

Amides result when NH_2 displaces OH of the COOH group in acids. Acetic acid is $CH_3{\cdot}CO{\cdot}OH$; hence *acetamide* is $CH_3{\cdot}CO{\cdot}NH_2$. Aniline boiled with glacial acetic acid yields *phenyl-acetamide*, or *acetanilide* (*Acetanilidum*, B.P.) or "*antifebrin*," $C_6H_5{\cdot}NH{\cdot}C_2H_3O$. Acetanilide is a febrifuge and a rival of "*antipyrin*," *phenyl-dimethyl-isopyrazolone*, or phenazone (*Phenazonum*, B.P.), $C_{11}H_{12}N_2O$, or $C_6H_5(CH_3)_2C_3HN_2O$, prepared by the interaction of phenylhydrazine or aniline and aceto-acetic ether. *Monobrom-acetanilide*, $C_6H_4Br{\cdot}NH{\cdot}C_2H_3O$, is a sedative and febrifuge. *Phenacetin* (*Phenacetinum*, B.P.) or *para-acetphenetidin*, $C_6H_4{\cdot}OC_2H_5{\cdot}NH{\cdot}C_2H_3O$, is another febrifuge. *Phenocoll* is *amido-acetphenetidin*, $C_6H_4{\cdot}OC_2H_5{\cdot}NHCOCH_2NH_2$. *Dulcin*, $NH_2CONH{\cdot}C_6H_4{\cdot}OC_2H_5$, or *para-phenetol-carbamide* is a substance possessing an exceedingly sweet taste, and has been proposed for use, like saccharin, in place of sugar.

Acetanilide occurs in "colourless, inodorous, glistening, lamellar crystals, having a slightly pungent taste. Melting-point, when dry, 236·5° F. (113·5° C.). It is soluble in 200 parts of cold or 18 parts of boiling *water*, and in 4 parts of *alcohol* (90 per cent.), freely soluble in *ether*, *benzol*, and *chloroform*. On boiling with *test-solution of ferric chloride* a reddish-brown colour is produced, and this is almost entirely discharged by *hydrochloric acid*. If acetanilide be heated with *solution of potassium hydroxide* until the odour of aniline is given off, and the liquid be then warmed with a few drops of *chloroform*, the unpleasant and penetrating odour of phenyl-isonitrile (isocyanide) is developed; and an aqueous solution mixed with *solution of bromine* gives a yellowish-white precipitate (distinctions from phenacetin). Heated with free access of air, it burns, leaving no residue. With *sulphuric acid* or with cold *nitric acid* it forms a colourless solution. A cold saturated aqueous solution does not affect *solution of litmus* (absence of free acid) and is not affected by *test-solution of ferric chloride* (absence of acetone, phenazone, and salts of aniline)."

Toluene, or Methyl-benzene (commercially known as *Toluol*), $C_6H_5CH_3$, forms the principal portion of the coal-tar distillate boiling between 100°-120° C.; it may be made synthetically by acting with sodium on a mixture of monochlorobenzene and methyl iodide.

$$C_6H_5Cl + CH_3I + 2Na = C_6H_5CH_3 + NaI + NaCl.$$

It is also obtained by the dry distillation of tolu balsam. It is an inflammable, highly refractive liquid, boiling at 111° C. It may be directly oxidized to benzoic acid.

$$2C_6H_5CH_3 + 3O_2 = 2C_6H_5COOH + 2H_2O.$$

Having both a phenyl (C_6H_5) and a methyl (CH_3) group in its molecule, it forms two sets of isomeric derivatives: one (*a*) in which, by acting on toluene in the cold, the atoms of hydrogen are displaced in the phenyl group, and the other (*b*) in which, by acting on boiling toluene, the atoms of hydrogen in the methyl group are displaced.

$$a\begin{cases}\text{Monochlorotoluene,} & C_6H_4Cl{\cdot}CH_3.\\ \text{Dichlorotoluene,} & C_6H_3Cl_2{\cdot}CH_3.\\ \text{Trichlorotoluene,} & C_6H_2Cl_3{\cdot}CH_3.\end{cases}$$

$$b\begin{cases}\text{Benzyl chloride,} & C_6H_5{\cdot}CH_2Cl.\\ \text{Benzylidene chloride,} & C_6H_5{\cdot}CHCl_2.\\ \text{Benzotrichloride,} & C_6H_5{\cdot}CCl_3.\end{cases}$$

Benzylidene chloride, $C_6H_5{\cdot}CHCl_2$, when acted on by glacial acetic acid and zinc chloride and water, yields benzaldehyde, C_6H_5COH (Jacobsen). By acting on benzotrichloride, $C_6H_5{\cdot}CCl_3$, with water in sealed tubes, benzoic acid results.

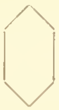
$$C_6H_5CCl_3 + 2H_2O = C_6H_5COOH + 3HCl.$$

Cymene, $C_{10}H_{14}$, para-methyl-isopropylbenzene,

$$C_6H_4(CH_3)(C_3H_7)$$

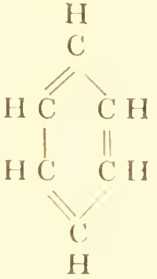
occurs in several volatile oils, and is readily obtained by the removal of hydrogen from the terpenes ($C_{10}H_{16}$) of those oils.

Constitution of the Benzene Series.



The facts that benzene forms three addition compounds with chlorine, $C_6H_6Cl_2$, $C_6H_6Cl_4$, and $C_6H_6Cl_6$, one molecule uniting with not more than six atoms of chlorine, and that it affords no isomeric monosubstitution derivatives (but only one toluene, $C_6H_5CH_3$, one benzoic acid, C_6H_5COOH, etc.), led Kekulé to represent benzene by the following figure (*a*), in which each carbon atom is assumed to be three-fourths linked to adjacent carbon atoms and one-fourth linked to hydrogen (the benzene ring):—

Fig. a.



Benzene

Fig. b.

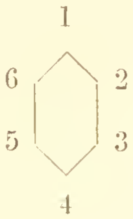
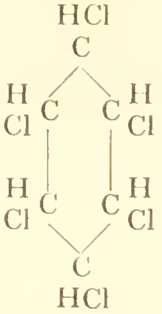


Fig. c.



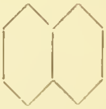
Benzene hexachloride

In a *monosubstitution derivative* such as chlorobenzene, C_6H_5Cl, no matter where the chlorine atom is represented, it always bears the same relation to the benzene nucleus; hence there can be *only one variety* of such a derivative. The experimental evidence of the truth of this inference is as follows. Displace H in benzene by a radical, X, and obtain C_6H_5X. In the latter displace H by Y and obtain C_6H_4XY. Now displace X by H and obtain C_6H_5Y. Lastly displace Y by X and obtain C_6H_5X. The first C_6H_5X and the second C_6H_5X are identical in properties, yet presumably the X in the latter is in a different position from that in the former; whence we conclude that actual position matters nothing if relative position is unchanged. Such hydrocarbons are *symmetrical*. Such mono-X compounds are *unsymmetrical*. Further displacement of H by X in C_6H_5X results in *more* *than one variety* of C_6H_4XX. In dichlorobenzene, $C_6H_4Cl_2$, the atoms of chlorine may (representing benzene, for the moment, by a hexagonal figure (*b*), and assuming that the carbon atoms are at the angles) be placed either at 1 and 2, 1 and 3, or 1 and 4, the chlorine atoms being linked to carbon atoms which are adjacent to each other in the benzene nucleus (ortho-position); separated from each other by one intervening carbon atom (meta-position); or separated from each other by two intervening carbon atoms (para-position). So with other *di-derivatives*. In trichlorobenzene, $C_6H_3Cl_3$, the atoms of chlorine may be placed at 1, 2, and 3; 1, 2, and 4; or 1, 3, and 5; 1, 2, and 4 being the same as 1, 3, and 4; 1, 2, and 3, the same as 1, 6, and 5, etc.; that is to say, the chlorine atoms must all three be linked to adjacent carbon atoms, or two may be linked to adjacent carbon atoms while one is linked to a carbon atom separated from these by an intervening carbon atom, or all three may be linked to carbon atoms which are separated from one another by intervening carbon atoms. So with other *tri-derivatives*. Hence, theoretically, there can only be three isomeric dichlorobenzenes and three trichlorobenzenes, and this has been verified by experiment. For other illustrations, *see* pp. 505, 506.

Benzene addition compounds.—The double linkages represented in the formula for benzene (fig. *a*), may be compared with those in the formulæ for olefines. As in the case of the olefines they indicate a condition of non-saturation and the capacity for forming addition compounds. It has been stated already (p. 469) that benzene can unite directly with two, four, or six atoms of chlorine: the product in the last case is benzene hexachloride, $C_6H_6Cl_6$ (fig. *c*). Other addition compounds can also be obtained, such as hexahydrobenzene, C_6H_{12}, which is formed when benzene is heated for some time at a temperature of 260° C. with hydriodic acid.

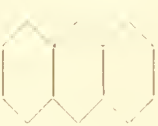
Other Series of Hydrocarbons

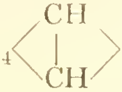
The Naphthalene Series, C_nH_{2n-12}.



Naphthalene, $C_{10}H_8$ (*Naphtalinum*, U.S.P.) is the chief member. It is a white crystalline substance, existing in coal tar. By oxidation it yields phthalic acid, $C_6H_4(COOH)_2$, the anhydride of which, $C_6H_4(CO)_2O$, fused with phenol, forms *Phenolphthalein*, B.P., used as an alkalimetric indicator. With other phenols various coloured compounds are produced; for example, with resorcinol *fluorescein*, which, treated with bromine, gives *eosin*. These compounds are termed *phthaleins*. Naphthalene is employed for increasing the luminosity of coal gas. Of the two *naphthyl alcohols*, α and β *naphthols* or *monoxynaphthalenes*, $C_{10}H_7(OH)$, *β-naphthol* is a powerful antiseptic, official in Britain and included in the United States Pharmacopœia (*Naphthol*, B.P. and Naphtol, U.S.P.).

The Anthracene Series, C_nH_{2n-18}.





$$C_6H_4\left\langle\begin{matrix}CH\\|\\CH\end{matrix}\right\rangle C_6H_4$$

Anthracene, $C_{14}H_{10}$ or $C_6H_4\left\langle\begin{matrix}CH\\|\\CH\end{matrix}\right\rangle C_6H_4$, is the only noteworthy member of this series, its importance being due to the fact that *artificial madder*, or *alizarin*, is formed from it by the following reactions:—Anthracene is first converted into anthraquinone, $C_{14}H_8O_2$ or $C_6H_4<^{CO}_{CO}>C_6H_4$, by oxidation. By acting on anthraquinone with fuming sulphuric acid, it is easily converted into a derivative, which yields potassium alizarate when fused with caustic potash.

Chrysophanic acid and the *aloins* are related to anthraquinone; chrysophanic acid being a dihydroxy-derivative of methylanthraquinone, and the aloins yielding on oxidation aloxanthin or tetrahydroxy-methylanthraquinone.

Chrysophanic Acid

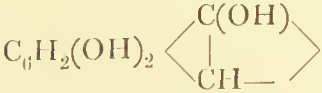
This yellow acid, $C_{15}H_{10}O_4$ or $C_6H_2(OH)_2<^{CO}_{CO}>C_6H_3CH_3$, is found in various species of rhubarb-root (*Rhei Radix*, B.P.) and, under the name of *parietinic acid*, in various common yellow lichens. Kubly and also Dragendorff consider that the chrysophanic acid of rhubarb is only produced when a glucoside, *chrysophan*, is acted on by a ferment in the presence of water. The formation of chrysophanic acid is probably, in most if not in all cases, preceded by the occurrence of *chrysophan*, or an allied substance. The author obtained it from araroba.

Chrysophanic acid may be obtained in crystals of a golden-yellow colour, hence the name (from χρυσὸς, *chrusos*, gold, and φαίνω, *phainō*, I shine). Its synonyms are *Rhaponticin*, *Rheic acid*, *Rheumin*, *Rhubarbaric acid*, *Rhubarbarin*, *Rumicin*. By the reducing action of hydriodic acid it yields chrysarobin. Chrysophanic acid, actual or potential, black and red-brown resins (*Aporetin*, *Phæoretin*), *Emodin*, *Rhein*, and a tannoglucoside are considered to be the conjoint source of the therapeutic properties of rhubarb. *Erythroretin* is merely a mixture of chrysophanic acid, emodin, and rhein. Chrysophanic acid and emodin (*see* below) are respectively di- and tri-oxymethylanthraquinone. Rhein ($C_{15}H_{10}O_6$, Hesse; $C_{15}H_8O_6$, Tschirsch and Heuberger) was regarded by Hesse as tetraoxymethylanthraquinone, but appears to conform rather to the second formula given above. Chrysophanic acid may also be obtained from several species of *Rumex* or dock. "Rumicin" is a preparation of yellow dock. *Cascara Sagrada*, or Sacred Bark (*Cascara Sagrada*, B.P.), according to Limousin, contains chrysophanic acid, a glucoside (?), and a ferment, various resins being also said to be present.

Emodin, $C_{15}H_{10}O_5$, as indicated above, is closely related to chrysophanic acid. It is obtained along with chrysophanic acid in the preparation of the latter from rhubarb. It also occurs in black alder bark, according to Liebermann and Waldstein. It is said to be derived, together with glucose, from *frangulin*, $C_{21}H_{20}O_9$, the glucoside of the dried bark.

Chrysarobin

This compound occurs in araroba (*Araroba*, B.P.), a substance found in cavities in the trunk of a leguminous tree (*Andira araroba*). Araroba is also known as Goa Powder, Bahia Powder, Brazil Powder, and Ringworm Powder. Chrysarobin (*Chrysarobinum*, B.P.), $C_{15}H_{12}O_3$ or



$$C_6H_2(OH)_2\left\langle\begin{matrix}C(OH)\\|\\CH-\end{matrix}\right\rangle C_6H_3CH_3,$$

is "obtained from Araroba by extracting with hot chloroform, evaporating to dryness, and powdering." By aerial oxidation in alkaline solution it is converted into chrysophanic acid.

Aloins

Aloins.—The aloes of pharmacy (*Aloe Barbadensis*, B.P., and *Aloe Socotrina*, B.P.) is an evaporated juice, doubtless much altered by the temperature to which it is subjected. It contains a yellow crystalline substance, *Aloinum*, B.P., perhaps slightly varying chemically, but not medicinally, as derived from the respective species of aloes. Aloin is not very soluble in cold water or alcohol, but readily soluble in these fluids on heating. Dissolved in alkalies it rapidly absorbs oxygen, but it is not readily altered in neutral or acid solutions.

Aloin may readily be obtained from either kind of aloes by warming the latter with three or four times its weight of amyl alcohol; pouring off the solution; allowing it to stand for a few hours to crystallize; and washing the deposited aloin with ether or carbon bisulphide to remove resinous matters.

Barbaloin.—This substance, first obtained by T. and H. Smith, occurs in minute crystals in Barbadoes aloes. It yields substitution compounds when acted on by bromine and chlorine. Boiled for some time with concentrated nitric acid, barbaloin gives, together with oxalic and picric acids, a yellow substance, chrysammic acid, which furnishes beautiful red salts (Tilden). Anthracene, $C_{14}H_{10}$, has been obtained by the reduction of barbaloin.

Isobarbaloin, $C_{21}H_{20}O_9$ (Léger), accompanies barbaloin in Barbadoes, Curaçao, and Jafferabad aloes. By oxidation with nitric acid it yields a substance apparently identical with chrysammic acid. It is much more easily oxidized than barbaloin, and with cold concentrated nitric acid it gives the red coloration (Klunge's reaction) hitherto attributed to barbaloin.

Nataloin.—This substance was discovered by Flückiger in Natal aloes. It crystallizes readily in rectangular plates, either from alcohol or from water. No bromine or chlorine substitution derivatives have yet been formed, but an acetyl compound has been analysed (Tilden). Nataloin moistened with nitric acid gives a red coloration which does not fade. When boiled with nitric acid it yields no chrysammic acid, but only oxalic and picric acids.

Homonataloin, $C_{22}H_{24}O_{10}$, occurs along with nataloin in Natal aloes. According to Léger it is a lower homologue of nataloin, from which it can be separated by fractional crystallization from methyl alcohol.

Socaloin or *Zanaloin.*—Histed and Flückiger have shown that Socotrine or Zanzibar aloes yields an aloin distinct from those just described. It forms tufted acicular prisms. Nitric acid scarcely alters the colour of socaloin. Neither socaloin nor barbaloin affords any colour when vapour from a glass rod moistened with nitric acid is allowed to come into contact with a drop of concentrated sulphuric acid containing a minute fragment of the aloin, while nataloin gives rise to a blue coloration.

E. von Sommaruga and Egger ("Pharmacographia") arrived at the conclusion that the aloins form an homologous series, and that they have the composition indicated in the following formulæ: Socaloin, $C_{15}H_{16}O_7$; Nataloin, $C_{16}H_{18}O_7$; Barbaloin, $C_{17}H_{20}O_7$. Tilden's subsequent experiments indicate, however, that barbaloin and socaloin are isomeric in the anhydrous state, but that socaloin and its derivatives in the hydrous condition contain more water of crystallization than barbaloin. Nataloin is less soluble than the other aloins. Its formula, according to Léger, is $C_{23}H_{26}O_{10}$. It does not yield either chrysammic acid or chloro- or bromo-derivatives. According to Groenewold the formula for the aloin from the aloes of Barbadoes and Curaçao is $C_{16}H_{16}O_7$, and that from Natal aloes $C_{24}H_{26}O_{10}$. The formula officially accepted for Barbaloin is $C_{16}H_{16}O_7$, $3H_2O$, but Léger (1903) gives it the formula $C_{21}H_{20}O_9$.

QUESTIONS AND EXERCISES

What is the formula of benzene? How is benzene artificially and commercially prepared?—Construct an equation explanatory of the production of aniline.—What is the relation between toluene and benzoic acid?—Give the formulæ of naphthalene and anthracene.—Explain by equations the production of alizarin or artificial madder.—Mention the colouring principle of rhubarb.—To what is rhubarb considered to owe its medicinal activity?—Give tests for distinguishing the aloins.

The student is referred to the accompanying table for a general view of the relations of four series of hydrocarbons (the paraffin, benzene, naphthalene, and anthracene series) to each other. Three members of the paraffin series are shown,

TABLE OF SHORT DIRECTIONS FOR APPLYING SOME OF THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS OR ONLY SLIGHTLY ACID SOLUTION OF ORDINARY SALTS OF ANY OF THE METALS OF GENERAL INTEREST.

Add hydrochloric acid.

<table>
<tr><td colspan="3">Precipitate
Hg(ous) Pb Ag
Wash, boil with water, filter.</td><td colspan="20">Filtrate
Cd Cu Hg(ic) Pb Bi As(ous)(ic) Sb Sn(ous)(ic) Zn Mn Co Ni Al Fe(ous)(ic) Cr Ba Sr Ca Mg Li K Na NH_4
Pass H_2S through the liquid, filter.</td></tr>
<tr><td colspan="2">Residue
Hg(ous) Ag
Wash, add NH_4OH.</td><td rowspan="5">Filtrate
Pb
Add H_2SO_4
White ppt.</td><td colspan="8">Precipitate
Cd Cu Hg(ic) Pb Bi As Sb Sn
Collect, wash, digest with NH_4SH and S, filter.</td><td colspan="12">Filtrate
Zn Mn Co Ni Al Fe Cr Ba Sr Ca Mg Li K Na NH_4
Add NH_4Cl, NH_4OH, and NH_4SH, warm gently, and filter.</td></tr>
<tr><td rowspan="4">Res.
Hg
(ous)
Black</td><td rowspan="4">Filtrate
Ag
Add
HNO_3.
White ppt.</td><td colspan="5">Precipitate
Cd Cu Hg(ic) Pb Bi
Wash, boil in HNO_3, filter.</td><td colspan="3">Filtrate
As Sb Sn
Add dilute HCl, filter, drain well, add concentrated HCl, boil, dilute slightly, filter.</td><td colspan="6">Precipitate
Zn Mn Co Ni Al Fe Cr
Collect, wash, dissolve in HCl, with a few drops of HNO_3, boil, add NH_4OH, stir, filter.</td><td colspan="6">Filtrate
Ba Sr Ca Mg Li K Na NH_4
Add $(NH_4)_2CO_3$, warm, filter.</td></tr>
<tr><td rowspan="3">Residue
Hg
(ic)
Black.
Confirm by Cu test in original solution.</td><td colspan="4">Filtrate
Cd Cu Pb Bi
Add NH_4OH, filter.</td><td rowspan="3">Residue
As
Yellow.
Confirm by Fleitmann's test.</td><td colspan="2">Filtrate
Sn Sb
Pour into H-apparatus.</td><td colspan="3">Precipitate*
Fe Al Cr
Wash, dry, fuse on Pt. foil with Na_2CO_3 and KNO_3, boil in water, and filter.</td><td colspan="3">Filtrate
Zn Mn Co Ni
Acidify with $HC_2H_3O_2$, pass H_2S, filter.</td><td colspan="3">Precipitate
Ba Sr Ca
Collect, wash, dissolve in $HC_2H_3O_2$, add excess of K_2CrO_4, filter.</td><td colspan="3">Filtrate
Mg Li K Na NH_4
Add $(NH_4)_2HPO_4$, stir, filter.</td></tr>
<tr><td colspan="2">Precipitate
Pb Bi
Wash, add a few drops HNO_3, dilute, filter.</td><td colspan="2">Filtrate
Cd Cu
Add KCy and H_2S.</td><td rowspan="2">Sn
remains on Zn.
Dissolve in HCl, and apply tests.</td><td rowspan="2">Sb
escapes as SbH_3.
Test as usual.</td><td rowspan="2">Residue
Fe_2O_3
brown.
Test original solution for ferrous or ferric state.</td><td colspan="2">Filtrate
If yellow, Cr present.
Divide into two parts.</td><td rowspan="2">Sol.
Mn
Add NH_4OH and NH_4SH
Buff, turning brown.
Search also for Mn in the Fe Al Cr ppt.</td><td colspan="2">Precipitate
Zn Co Ni
Boil with HCl and a little HNO_3; add KOH, filter.</td><td rowspan="2">Ppt.
Ba
Yellow</td><td colspan="2">Filtrate
Sr Ca
Add dilute H_2SO_4, let stand, filter.</td><td rowspan="2">Ppt.
Mg
White</td><td colspan="2">Filtrate
Li K Na NH_4
Evaporate to small bulk, add NH_4OH.</td></tr>
<tr><td>Ppt.
Bi
White.
<i>See</i> also pp. 279 and 280.</td><td>Filt.
Pb
Add H_2SO_4, set aside; white ppt.
<i>See</i> footnote to p. 270.</td><td>Ppt.
Cd
Yellow.</td><td>Filt.
Cu
Acidify with $HC_2H_3O_2$
Brown ppt.</td><td>Sol.
Al
Add excess of NH_4Cl and boil off NH_3.
White ppt.</td><td>Sol.
Cr
Add $HC_2H_3O_2$ and excess of $AgNO_3$; red ppt.
Or boil with H_2SO_4 and alcohol.
Green sol.</td><td>Filt.
Zn
Add NH_4SH.
White ppt.</td><td>Precipitate
Co Ni
Dissolve in HCl and proceed as directed on p. 156.</td><td>Ppt.
Sr
White</td><td>Filt.
Ca
Add NH_4OH and $(NH_4)_2C_2O_4$
white ppt.</td><td>Ppt.
Li
<i>See</i> p. 281.</td><td>Filtrate
K Na NH_4
Evaporate, ignite, dissolve.
Test for K by H_2PtCl_6, or by Carnot's test, p. 82,
Na by flame,
NH_4 in original solution.</td></tr>
<tr><td colspan="3"><i>See</i> also p. 278.</td><td colspan="5"></td><td colspan="3"><i>See</i> also p. 279.
Au and Pt are specially sought when necessary.</td><td colspan="3"><i>See</i> also p. 280.
* Test this also for Mn by Crum's process, p. 151.</td><td colspan="3"></td><td colspan="3"><i>See</i> also page 281, and the more delicate separation given on p. 136.</td><td colspan="3"></td></tr>
</table>

[*To face p.* 276.]

two of the benzene series, and one each of the naphthalene, and anthracene series. Beneath each hydrocarbon are given some examples of its chief derivatives. A glance along the table shows the relation of these derivatives to each other.

THE TERPENE SERIES OF HYDROCARBONS

The terpene series have the general formula, C_nH_{2n-4}. *Terebenthene* or *pinene* $C_{10}H_{16}$ (pure oil of turpentine), is the most common member of the series.

The hydrocarbons called terpenes, $C_{10}H_{16}$, are very commonly met with as constituents of the volatile oils. Very few of these oils have been produced artificially. Their fragrance is chiefly due to the non-terpenoid constituents (Wallach). They differ from one another in the extent to which they rotate the plane of polarization of light, and also in the sense of the rotation (*i.e.*, right or left). They may be divided into classes, of which several are interesting in pharmacy: (*a*) *Terpenes* or *pinenes*, boiling at about 156° C., and found in ordinary turpentine and other volatile oils; (*b*) *sylvestrene*, found in Russian and Swedish turpentine; (*c*) *phellandrene*, lævo-rotatory (left-rotating) from *Phellandrium aquaticum*, and dextro-rotatory (right-rotating) from the *E. amygdalina* variety, chiefly, of *Eucalyptus* oils (p. 542), boiling-point 170° C.; (*d*) *citrenes* (*limonenes*), boiling at about 175° C., and derived from the different species of citrus; (*e*) *dipentene*, found in some turpentines and oils of camphor and elemi; (*f*) *terpinene*, occurring in oil of cardamoms. *Camphene*, *fenchene*, and *terpinolene* are terpenes, camphene occurring naturally in certain oils. The *sesquiterpenes* have the formula $C_{15}H_{24}$ and include *cadinene*, found in oils of cubebs, savin, cade, betel, camphor, galbanum, patchouli, juniper, asafetida, hop, and olibanum; *caryophyllene*, found in oil of cloves; and other isomers of these. They boil at a much higher temperature than the terpenes, but resemble them in other respects.

Oil of *Turpentine* (*Oleum Terebinthinæ*, B.P.). Turpentine itself is really an oleo-resin of about the consistence of fresh honey. It flows naturally or by incision from the wood of most coniferous trees; larch (*Pinus Larix*) yielding *Venice*

Turpentine, Abies balsamea furnishing *Canadian Turpentine* or *Canada Balsam* (*Terebinthina Canadensis*, B.P.), the *bark* of *Pistachia terebinthus*, the variety termed *Chian Turpentine* (containing about 1 part of essential oil to 7 of resin), and *Pinus australis* (*palustris*), *P. Abies*, *P. pinaster* and *P. tæda*, affording the common American Turpentine. *Pinus maritima* gives the French or Bordeaux Turpentine, and *P. picea* the old fragrant Strasburg Turpentine. By distillation with steam, the crude turpentine is separated into *colophony, rosin*, or *resin*, which remains in the still, and *essential oil of turpentine*, often termed simply *turpentine, spirit of turpentine*, or "*turps*," which distils over. Mixed with alkali to saturate resinous acids, and redistilled in a current of steam, oil of turpentine furnishes about 80 per cent. of *rectified oil of turpentine*. *Pinus sylvestris* and *P. Ledebourii* furnish Russian turpentine (which, according to Tilden, consists of two terpenes and cymene) and also (Wallach) a left-rotating limonene. This turpentine is probably a by-product in the preparation of common *wood tar* (*Pix Liquida*, B.P.); its odour is very pleasant, quite different from that of ordinary turpentine. The leaves of the *Pinus sylvestris*, or Scotch fir, are in Germany broken down to a woolly condition, producing Pine Wool or Fir Wool, or wadding used in making vermin-repelling blankets; and this substance, or, still better, the fresh leaf, by distillation with water, yields *Fir-Wool Oil*, consisting, according to Tilden, of two terpenes, like those of Russian turpentine, and cymene. The oil distilled from the fresh leaves of *Pinus Pumilio* is official (*Oleum Pini*, B.P.). The terpene of Bordeaux turpentine (terebenthene) rotates the plane of the polarization of light more than the terpene of American turpentine, and in the opposite sense—*i.e.*, to the left.

Turpentine "commences to boil at about 320° F. (160° C.), and almost entirely distils below 356° F. (180° C.), little or no residue remaining," whereas petroleum spirit, with which turpentine might be mixed, covers a much wider range of temperature during its distillation. Petroleum spirit also, when the small round flame of the end of a piece of twine is brought near to some of the spirit in a cup, gives a momentary flash of flame at a much lower temperature than that at which turpentine flashes. Tested in the specially arranged flash-point apparatus of the last Petroleum Act, Boverton Redwood found that the flash-point of turpentine was lowered 10° F., by 1 per cent. of petroleum spirit. The specific gravity of oil of turpentine is from about 0·855 to 0·870.

Under the influence of heat and sulphuric acid or other chemical agents, pure oil of turpentine, $C_{10}H_{16}$, yields many derivatives of considerable chemical interest. Amongst them are two optically inactive terpene isomers named *terebene* and *colophene*, used for inhalation and as disinfectants and deodorizers. When acted on by gaseous hydrochloric acid, the product is a white crystalline monohydrochloride, $C_{10}H_{16}HCl$. In sunlight and in presence of moisture it slowly undergoes oxidation and hydrolysis, forming a crystalline substance, $C_{10}H_{18}O_2$. Bromine acts violently on turpentine and terpenes, giving rise to dibromides which yield cymene when heated, $C_{10}H_{16}Br_2 = C_{10}H_{14} + 2HBr$. Crystals of *terpin hydroxide*, $C_{10}H_{18}(OH)_2,H_2O$, also *terpinol* $(C_{10}H_{16})_2,H_2O$, are used therapeutically instead of terebene. The official terebene (*Terebenum*, B.P.), is "a mixture of dipentene and other hydrocarbons." "Not more than 15 per cent. should distil below 329° F. (165° C.)." *Terebenum*, U.S.P., "boils at 312° to 320° F."

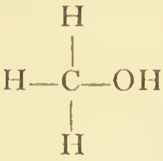
ALCOHOLS

Alcohols are the substances produced when one or more hydrogen atoms of the hydrocarbons are displaced by one or more hydroxyl (OH) groups, forming (*a*) monohydroxyl derivatives (monohydric or monatomic alcohols), (*b*) dihydroxyl derivatives (dihydric or diatomic alcohols), etc.; they are in fact hydroxides of hydrocarbon radicals, just as caustic potash, slaked lime, etc., are hydroxides of metallic radicals, thus:—

C_2H_5OH Ethyl hydroxide	KOH Potassium hydroxide
$C_2H_4(OH)_2$ Ethylene hydroxide, or glycol	$Ca(OH)_2$ Calcium hydroxide
$C_3H_5(OH)_3$ Glyceryl hydroxide, or glycerin	$Bi(OH)_3$ Bismuth hydroxide

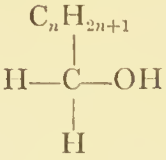
Monohydroxyl Derivatives of Hydrocarbons; Monohydric or Monatomic Alcohols.

The Ethyl Series of Alcohols, $C_nH_{2n+1}OH$.—The alcohols, or *carbinols* (Kolbe), are *primary*, *secondary*, or *tertiary*, according as the hydroxyl group is linked to a primary, a secondary, or a tertiary carbon atom (*see* p. 439). Thus:—



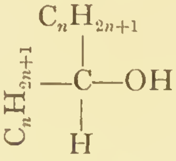
$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -OH \\ & | & \\ & H & \end{array}$$

Carbinol



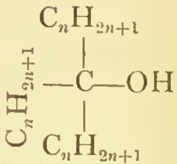
$$\begin{array}{ccc} & C_nH_{2n+1} & \\ & | & \\ H- & C & -OH \\ & | & \\ & H & \end{array}$$

Typical primary carbinol



$$\begin{array}{ccc} & C_nH_{2n+1} & \\ & | & \\ C_nH_{2n+1}- & C & -OH \\ & | & \\ & H & \end{array}$$

Typical secondary carbinol



$$\begin{array}{ccc} & C_nH_{2n+1} & \\ & | & \\ C_nH_{2n+1}- & C & -OH \\ & | & \\ & C_nH_{2n+1} & \end{array}$$

Typical tertiary carbinol

On oxidation, primary alcohols yield first aldehydes and then acids, the CH_2OH group of an alcohol becoming COH in the aldehyde, and COOH, or *carboxyl*, in the acid; secondary alcohols yield ketones, the CHOH group becoming CO, or *carbonyl* (as in acetone $CH_3-CO-CH_3$), and by further oxidation break up, forming acids with fewer carbon atoms than the original alcohol; while the tertiary yield a ketone and an acid. The primary alcohols alone are of practical interest to medical and pharmaceutical students. The tertiary alcohols are said to be depressants instead of stimulants. For examples of primary, secondary, and tertiary alcohols, *see* pp. 491, 492.

General method of preparing Primary Alcohols.—By acting on the monochloro-derivative of a paraffin with potassium or silver acetate, an ethereal salt (or ester) is produced, which when saponified with caustic potash yields the alcohol. For instance,—

$$\underset{\substack{\text{Ethyl}\\\text{chloride}}}{C_2H_5Cl} + \underset{\substack{\text{Silver}\\\text{acetate}}}{AgC_2H_3O_2} = \underset{\substack{\text{Ethyl}\\\text{acetate}}}{C_2H_5C_2H_3O_2} + \underset{\substack{\text{Silver}\\\text{chloride}}}{AgCl}$$

$$\underset{\substack{\text{Ethyl}\\\text{acetate}}}{C_2H_5C_2H_3O_2} + \underset{\substack{\text{Potassium}\\\text{hydroxide}}}{KOH} = \underset{\substack{\text{Ethyl}\\\text{alcohol}}}{C_2H_5OH} + \underset{\substack{\text{Potassium}\\\text{acetate}}}{KC_2H_3O_2}$$

If the chloro-derivatives were directly acted upon by the potassium hydroxide, hydrocarbons of the olefine or acetylene series would result.

The chief primary alcohols are ordinarily obtained otherwise than by the above general method.

Methyl Alcohol

Methyl (*μέθυ, methu,* wine, and *ὕλη, ule,* wood) Alcohol, or Carbinol, Methyl Hydroxide, CH_3OH, is a product of the destructive distillation of wood, occurring in *Pyroxylic Spirit* or *Wood Naphtha,* and is now obtained in large quantities as a by-product in the manufacture of beet sugar. By oxidation it yields formic acid (*see* p. 371).

Methylated Spirit.—Alcohol of about 84 per cent. strength, containing 10 per cent. by volume of wood naphtha, constitutes *methylated spirit,* a spirit issued duty free, for the use of manufacturers, the methyl alcohol, etc., not interfering with certain technical applications. Since 1891, the Regulations of the Inland Revenue authorities require that methylated spirit which is to be retailed to the public, in addition to the above proportion of wood naphtha, shall contain not less than three-eighths of one per cent. by volume of mineral naphtha (*i.e.,* coal-tar naphtha). This requirement is designed to prevent effectually the use of the mixture as a beverage, the addition of the mineral naphtha rendering it nauseous and unpalatable.

Detection of Methyl Alcohol in presence of Ethyl Alcohol.—Three or four methods have been proposed for the detection of methyl alcohol in alcoholic liquids, in the preparation of which methylated spirit should not be used; that most used by pharmacists is by J. T. Miller. For the application of the test to tinctures and similar alcoholic mixtures, some of the alcohol is first separated by distilling off a drachm or so from about half an ounce of the liquid placed in a small flask or a test-tube having a long bent tube attached. Into a similar apparatus put 30 grains of powdered potassium bichromate, half an ounce of water, 25 minims of concentrated sulphuric acid, and 30 or 40 minims of the distillate to be tested. Set the mixture aside for a quarter of an hour, and then distil nearly half a fluid ounce. Place this distillate in a small dish, add a very slight excess of sodium carbonate, boil down to about a quarter of an ounce, add enough acetic acid to impart a feeble but distinct acid reaction, pour the liquid into a test-tube, add a grain of silver nitrate dissolved in about 30 minims of water, and heat gently for a couple of minutes. If the liquid then merely darkens a little, but continues quite translucent, the spirit is free from methyl alcohol; but if a copious precipitate of dark-brown or black metallic silver separates, and the tube, after being rinsed out and filled with water, has a distinct film of silver adhering to it, which appears brown by transmitted light (seen by holding it against white paper), the spirit is methylated. The experiments are best performed by daylight.

This test depends for its action on the reducing-powers of formic acid. In the above operation the ethyl alcohol becomes oxidized to acetic acid (the corresponding acid of the ethyl series), which does not reduce silver salts, a minute quantity only of formic acid being produced, while the methyl alcohol yields formic acid (the corresponding acid of the methyl series) in a comparatively large quantity. Aldehyde, which is also a reducing agent, is simultaneously produced, but is removed in the subsequent ebullition with sodium carbonate.

Methylated Sweet Spirit of Nitre.—The preparation of spirit of nitrous ether from methylated spirit is illegal in Great Britain, and, probably, is very rarely practised. For the detection of methyl alcohol in this liquid, Miller suggests the following modification of the foregoing process.

Shake about an ounce of the sample with 20 or 30 grains of dry potassium carbonate, and, if needful, add fresh portions of this salt as long as it continues to be dissolved, then pour off the supernatant liquid. This treatment serves to neutralize acid and to remove water, of which an abnormal quantity may be present. Introduce half a fluid ounce of the prepared liquid into a small flask; add 150 grains of dry calcium chloride in powder, and stir well together; then, having connected the flask with a condenser, place it in a bath of boiling water, and distil a fluid drachm and a half, or continue the distillation until scarcely anything more comes over. The operation is rather slow, but needs little attention, and should be done thoroughly. The distillate contains nearly the whole of the nitrous ether and other interfering substances, while in the retort there remains a non-volatile compound of calcium chloride and methyl alcohol, if the latter be present. Now add to the contents of the flask a fluid drachm of water, which decomposes the compound just referred to, and distil over the half drachm of liquid required for testing. Then proceed as already described.

Ethyl Alcohol

Ethyl Alcohol, or Methyl Carbinol, Ethyl Hydroxide, commonly called simply *Alcohol*, C_2H_5OH, or CH_3CH_2OH.—It is a colourless liquid, having a boiling-point of 172·9° F. (78·3° C.) and sp. gr. 0·7935. Ethyl alcohol may be obtained by passing ethylene into concentrated sulphuric acid and distilling the product, ethyl hydrogen sulphate, with water :—

$$C_2H_4 + H_2SO_4 = C_2H_5HSO_4$$
$$C_2H_5HSO_4 + H_2O = C_2H_5OH + H_2SO_4$$

On the large scale alcohol is produced by fermentation of certain kinds of sugar. All fermented bread retains a little alcohol, sometimes as much as 1 in 400.

Experiment.—Dissolve two or three grains of sugar in a test-tubeful of water, add a little yeast (a piece of the so-called German or dried yeast may be used), and set the tube aside for several hours in a warm place at a temperature of 75° to 85° F. (23·8° to 29·4° C.). Carbonic anhydride is evolved, and, if the tube be inverted in a small dish containing water, may be collected in the upper part of the tube and subsequently tested : the solution contains alcohol. If the experiment be made on larger quantities (four ounces of sugar, one of yeast, and a pint of water) the fermented liquid should be distilled, one-half being collected, shaken with a little lime, caustic soda, or potash to neutralize any acetic acid and decompose ethereal salts, and again distilled till one-half has passed over ; the product is dilute alcohol. It may be still further concentrated or rectified by repeated similar fractional distillations. Stills can be so constructed, especially on the large scale, as to condense and separately deliver the substances having different boiling-points.

Fermentation.—The change known as fermentation is commonly the result of some vital action. *Alcoholic fermentation* would appear always to result from the development of a living vegetable organism and the free multiplication of its cellular structure. This organism is the yeast plant, *Saccharomyces cerevisiæ.* In the presence of this plant, with small quantities of phosphates and albumenoid matter, *glucose* is converted into alcohol and carbonic anhydride, together with small proportions of glycerin, succinic acid, and other substances. Cane sugar, or *sucrose*, does not itself undergo alcoholic fermentation. It can, however, by various methods, be converted into glucose which is fermentable. Yeast contains a soluble ferment, *invertase*, which is capable of converting sucrose into glucose, so that by the action of yeast cane sugar may be converted into carbonic anhydride and alcohol, the soluble ferment first converting the sucrose into glucose. It has recently been shown that the action of the yeast plant upon glucose is also due to a soluble ferment or enzyme contained in the cell and termed *zymase.*

$$\underset{\text{Glucose}}{C_6H_{12}O_6} = \underset{\text{Alcohol}}{2C_2H_5OH} + \underset{\text{Carbonic anhydride}}{2CO_2}$$

Not more than 20 per cent. by weight of alcohol can be obtained in a fermenting liquid, since alcohol itself prevents fermentation when present in larger proportion than this in a liquid which otherwise would be capable of undergoing the change.

Other kinds of fermentation, arising from the action of special ferments which have not received in all cases distinctive names, are the following:—*Viscous* or *Mannitic fermentation*, which occurs when beer or saccharine juices, such as that of beet-root, become "ropy." Gum, mannite, and carbonic anhydride, are produced. For *Lactic* and *Butyric fermentations, see* pp. 379 and 526. *Putrefactive fermentation* occurs when a liquid containing albumenoid matter is exposed to the air. Infusoria appear in the liquid, using up the dissolved oxygen, and the ferments of the genus *vibrio* are developed. These are protected from oxygen, which is fatal to them, by a thin surface layer crowded with *bacteria*—small rod-like organisms having in some cases powers of locomotion. The putrefaction proceeds with evolution of hydrogen sulphide, methane, and hydrogen, together with other gases having unpleasant odours and of complex chemical constitution. For *Acetic fermentation, see* "Acetic Acid." For *Ammoniacal fermentation, see* "Urine."

Fermentation by certain Soluble Ferments or Enzymes.—For the conversion of starch into sugar by diastase, *see* "Starch"; of amygdalin into benzoic aldehyde, hydrocyanic acid, and glucose by emulsin, *see* "Amygdalin"; of salicin into saligenin and glucose, *see* "Salicin"; of potassium myronate into allyl iso-thiocyanate, etc., by myrosin (*see* p. 494); of cane-sugar into grape-sugar by the soluble ferment in yeast, *see* the foregoing paragraphs. Many soluble ferments or *enzymes* occur in the germinating seeds and other parts of plants, and play an important part in nutrition.

The nomenclature of ferments and fermentation is now emerging from early confusion. The word *fermentation* originally described the action that goes on in the preparation of alcoholic liquids or of dough, for it is derived from the Latin *ferveo*, I boil, or seethe, in allusion to the evolution of gas. But discoveries of ferments have so multiplied as to force classification, resulting in the names *organised ferments* (yeast, for example), and *unorganised ferments* (such as diastase); the latter are also termed *soluble ferments* or *enzymes*. Moreover to the action of many so-called ferments the word *fermentation* is scarcely applicable, as, though otherwise strictly analogous to fermentation, no gas is given off. Hence the word *zymosis* (from ζύμωσις, *zumosis*, fermentation) for the action of organised ferments, while the soluble or unorganised ferments are termed *enzymes*, and their action one of *zymolysis*.

Alcoholic Fermentation.—On the large scale the operation of alcoholic fermentation is carried out by the action of yeast upon maltose, a variety of sugar produced from the starch present in the seeds of cereals. During germination the starch of the grain, under the influence of a ferment called diastase which is also present, is converted into dextrine and maltose. The chief reaction during fermentation results, as already stated, in the formation of alcohol and carbonic anhydride, though 3 per cent. of glycerin, 0·5 of succinic acid, and traces of several other substances are simultaneously produced (*see* "Fusel Oil," p. 492). By the fermentation of various fruit juices and other saccharine liquids there is produced the alcohol present in the different kinds of wine and beer as well as in brandies, liqueurs, and distilled spirits generally. Orange Wine (*Vinum Aurantii*, B.P.), is made "by the fermentation of a saccharine solution to which Fresh Bitter-Orange Peel has been added"; Sherry Wine (*Vinum Xericum*, B.P.), is the fermented juice of the grape; Bay Rum or Spirit of Myrcia (*Spiritus Myrciæ*, U.S.P.), is made by distilling rum with leaves of *Myrcia acris* and other plants, or by dissolving their oils in alcohol; and so on.

Alcoholic beverages vary much in strength. Cider or apple-wine, perry or pear-wine, and good beer (ale and porter or stout) contain 4 to 7 per cent. by volume of alcohol; good light wines, both "red" and "white," and natural sherry, 10 to 12 per cent.; strong sherry and port, which are commonly "fortified," that is, contain added spirit, 16 or 18 per cent.; while "spirits" (gin, rum, brandy, whisky, etc.), and "liqueurs" (ratafia, almond-flavoured; maraschino, cherry-flavoured; curaçoa, orange-flavoured; chartreuse, a composite-flavoured liqueur, etc.), are "under-proof" or "over-proof," terms explained in a following paragraph. Vermouth is an infusion of bitter and aromatic herbs and roots in white wine. For excise purposes "beer" is any such liquid or substitute which contains more than 2 per cent. of proof spirit. The well-known effects of these spirituous fluids on the animal system would appear to be due primarily to alcohol, and secondarily to esters. Some owe a part of their effect to non-volatile substances, for beer from which all alcohol, etc., has been removed by ebullition is said to have considerable effect on the human economy.

Spirit of French Wine (*Spiritus Vini Gallici*, B.P.) or *Brandy* is a coloured and flavoured variety of alcohol distilled from French wine. Its colour is that of light sherry, and is derived from the cask in which it has been kept, but is commonly deepened by the addition of burnt sugar. Its taste is due to the volatile flavouring constituents of the wine, often increased by the addition of artificial essences.

Ethyl Alcohol of various strengths.—A liquid containing 85·65 per cent. *by weight* of pure alcohol, and 14·35 per cent. by weight of water, constitutes the official "Alcohol (90 per cent.)" (*Spiritus Rectificatus*, B.P.). Its sp. gr. is 0·8340. It contains "90 parts *by volume* of ethyl hydroxide, C_2H_5OH, and 10 parts by volume of water." With four different proportions of added water, it forms the four official liquids known as Diluted Alcohols, viz.:—1. Alcohol (70 per cent.), sp. gr. 0·8900; 2. Alcohol (60 per cent.), sp. gr. 0·9135; 3. Alcohol (45 per cent.), sp. gr. 0·9436; 4. Alcohol (20 per cent.), sp. gr. 0·9760: these percentages being by volume.

A mixture of alcohol and water containing 84 per cent. by weight of pure alcohol, constitutes common *spirit of wine*: its sp. gr. is 0·8382. It was formerly official as *rectified spirit.*

Another mixture containing 49·25 per cent. by weight, 57 by volume, of pure alcohol, is known as *proof spirit,** and was formerly official; its sp. gr. is 0·920 (actually 0·91984). In the language of the Excise authorities, the official Alcohol (90 per cent.) would be described as "58 degrees over-proof" (58 O.P.); that is, 100 volumes contain as much alcohol (ethyl hydroxide) as is present in 158 volumes (nearly) of proof spirit. Obviously, proof spirit may be made by diluting rectified spirit of any strength with water. Thus 100 fluid ounces of a spirit of "70 over-proof" may be diluted to 170, or the same quantity of a spirit of "50 over-proof" may be diluted to 150, and so on. Spirit of 10 per cent. "under-proof" contains as much alcohol as would be present in spirit formed of 90 volumes of proof spirit mixed with sufficient water to form 100 volumes. According to British law, gin is not "adulterated" with water if it is not weaker than 35 degrees under-proof; nor brandy, whisky, or rum, if they are not weaker than 25 degrees under-proof.

Inland Revenue regulations, dated November 1902, permit the use of ethyl alcohol of various strengths and of pure methyl alcohol, *duty-free,* for purposes of teaching and research in Universities, Colleges, etc.

Absolute Alcohol, C_2H_5OH (*Alcohol Absolutum,* B.P.), may be prepared by the removal of water from less strong ethyl alcohol. This can be accomplished, partially, by means of dry potassium carbonate, and more completely by means of recently fused calcium chloride. In operating on, say, one pint, 2 ounces of dry potassium carbonate should be placed in a bottle that can be well closed, and frequently shaken during two days with the spirit. Meanwhile put rather more than a pound of calcium chloride into a covered crucible, and subject it to a red heat for half an hour; then pour the fused salt on to a clean stone slab, cover it quickly with an inverted porcelain dish, and when it has solidified, break it up into small fragments, and enclose it in a dry stoppered bottle. Put one pound of this fused calcium chloride into a flask, pour over it the spirit decanted from the potassium carbonate, and closing the mouth of the flask with a cork, shake them together and allow them to stand for twenty-four hours with repeated agitation. Then attaching a dry condenser closely connected with a receiver from which free access of air is excluded, and applying the flame of a lamp to the flask, distil about two fluid ounces, which should be returned to the flask, after which the distillation is to be continued until fifteen fluid ounces have been recovered. The product should be colourless and free from empyreumatic odour; its specific gravity should be from 0·794 to 0·7969, and it should contain not more than 1 per cent. by weight of water. It is entirely volatilized by heat, is not rendered turbid when mixed with water, does not cause anhydrous cupric sulphate to assume a blue colour even after the two have been well shaken together. What little water remains may, if necessary, be removed by the cautious addition of metallic sodium in small quantity. If 5 per cent. of sodium be used, solution of sodium ethylate, or caustic alcohol (*Liquor Sodii Ethylatis*, B.P.) results by replacement of the hydroxyl hydrogen by sodium:—$2Na + 2C_2H_5OH = 2C_2H_5ONa + H_2$. The solution contains 18 per cent. of sodium ethylate.

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* *Proof spirit* is so termed from the fact that in olden times a proof or test of its strength was afforded by moistening with it a small quantity of gunpowder and setting light to the spirit; if it fired the powder, it was said to be "over-proof"; if not, "under-proof." The weakest spirit that would stand this test was what we should now describe as of sp. gr. 0·920.

The most highly purified ethyl alcohol obtainable has sp. gr. 0·7935 at 60° F. (15·5° C.), and boils at 78·3° C.

Tests.—There are no specific tests for alcohol when mixed with complex matters. It is, however, easily isolated and concentrated by fractional distillation, and is then recognisable by noting its physical and chemical characters. Thus its odour and taste are characteristic; it is lighter than water, volatile, colourless, and when tolerably strong, inflammable, burning with an almost non-luminous flame; it readily yields aldehyde (*see* p. 520) and acetic ether (*see* p. 465), each of which has a characteristic odour; and in hot acid solutions, alcohol reduces potassium bichromate to a green chromic salt.

According to Lieben, 1 part of alcohol in 2000 of water can be detected by adding to some of the warmed liquid a small quantity of iodine, a few drops of solution of caustic soda, again warming gently, and setting aside for a time; a yellowish crystalline deposit of *iodoform*, CHI_3, is obtained.

Under the microscope the latter presents the appearance of hexagonal plates or six-rayed and other varieties of stellate crystals.

$$C_2H_6O + 4I_2 + 6NaOH = CHI_3 + NaCHO_2 + 5NaI + 5H_2O$$

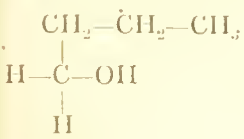
Other alcohols, aldehydes, gum, turpentine, sugar, and several other substances give a similar reaction.

Tests of Purity.—Oil or resin is precipitated on diluting alcohol containing it with distilled water, giving an opalescent appearance to the mixture. Fusel oil, aldehyde, and such impurities are detected by means of silver nitrate (*see* the official test of purity on p. 732). Water in absolute alcohol may be detected by adding to a small quantity some highly dried cupric sulphate, which becomes blue ($CuSO_4, 5H_2O$) if water be present, but retains its yellowish-white appearance ($CuSO_4$) if water be absent.

Note.—Most ethyl derivatives are formed from alcohol, for example, the ethyl nitrite in spirit of nitrous ether, ethyl iodide, etc., which have already been described. On oxidation alcohol yields aldehyde and acetic acid.

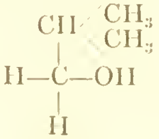
Propyl and Butyl Alcohols

The primary and secondary propyl alcohols, $C_2H_5CH_2OH$ and $(CH_3)_2CHOH$, and the four isomeric butyl alcohols, C_4H_9OH (see below), are of little pharmaceutical interest.



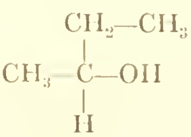
$$\begin{array}{c} CH_2-CH_2-CH_3 \\ | \\ H-C-OH \\ | \\ H \end{array}$$

Primary normal butyl alcohol



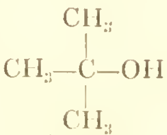
$$\begin{array}{c} CH\begin{matrix} CH_3 \\ CH_3 \end{matrix} \\ | \\ H-C-OH \\ | \\ H \end{array}$$

Primary iso-butyl alcohol



$$\begin{array}{c} CH_2-CH_3 \\ | \\ CH_3-C-OH \\ | \\ H \end{array}$$

Secondary butyl alcohol



$$\begin{array}{c} CH_3 \\ | \\ CH_3-C-OH \\ | \\ CH_3 \end{array}$$

Tertiary butyl alcohol

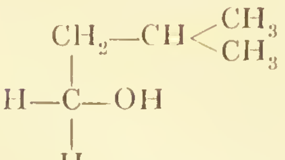
The new hypnotic known as *chloretone* is a trichloro-derivative of tertiary butyl alcohol. Its formula is $CCl_3(CH_3)_2C{\cdot}OH$.

Amyl Alcohols

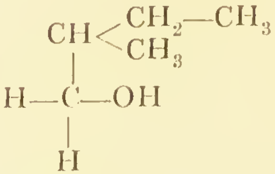
Amyl Alcohol, $C_5H_{11}OH$, or $C_4H_9CH_2OH$, is always produced during the preparation, by fermentation, of ethyl or common alcohol, C_2H_5OH, especially when the latter is prepared from sugar which has been derived from starch;

hence the name, from *amylum*, starch. The sugar from potato-starch yields a considerable quantity; hence the alcohol is often called *potato oil*. The impure amyl alcohol obtained and separated during the preparation of common alcohol is also termed *fousel oil* or *fusel oil* (from φύω, *phuo*, to produce), in allusion to the circumstance that the so-called oil is not simply educed from a substance already containing it (as is usually the case with oils), but is actually produced during the operation. It was described as oil probably because it resembled oil in not readily mixing with water; but it is soluble to some extent in water, and is an alcohol homologous with ethyl alcohol. It often contains variable proportions of propyl, butyl, and capryl alcohols. (*See* also Valerianic Acid.) It should be redistilled for medicinal use and the product passing over at 262° to 270° F. (or about 128° to 132° C.) should alone be collected.

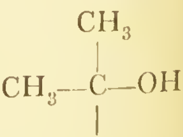
Purified fusel oil is a colourless liquid, with a penetrating and oppressive odour and a burning taste. It is sparingly soluble in water, but soluble in all proportions in alcohol, ether, and essential oils. Exposed to the air in contact with platinum black, it is slowly oxidized, yielding valerianic acid, $C_4H_9{\cdot}COOH$. Eight isomeric varieties of amyl alcohol are known, of which three possess pharmaceutical interest. Two of these, viz., primary inactive iso-amyl alcohol or iso-butyl carbinol and primary active amyl alcohol, are present in purified fusel oil, the former constituting much the larger proportion of it: the third isomeric variety is tertiary amyl alcohol.



Primary
inactive
iso-amyl alcohol



Primary
active
amyl alcohol



$$\begin{array}{c} CH_3 \\ | \\ CH_3\!-\!C\!-\!OH \\ | \\ C_2H_5 \end{array}$$

Tertiary
amyl alcohol
"Amylene hydrate"

The constitution of the variety of amyl alcohol termed *tertiary amyl alcohol*, or *dimethyl-ethyl-carbinol*, is shown in the above graphic formula. It is used in medicine in place of chloral hydrate, and is known as amylene hydrate.

Other Monohydric Alcohols

Among the higher alcohols of the ethyl series are the following:—

Cetyl Alcohol or *Cetyl Hydroxide,* $C_{16}H_{33}OH$, formerly termed *ethal,* obtained by saponifying spermaceti (*Cetaecum,* B.P.), which consists of cetyl palmitate, $C_{16}H_{33}C_{16}H_{31}O_2$, or *cetine.* Spermaceti is the solid crystalline fat accompanying sperm-oil in the head of the sperm whale.

Ceryl Alcohol, $C_{27}H_{55}OH$, is obtained in a similar manner from Chinese-wax (ceryl cerotate).

Melissyl Alcohol or *Myricyl Alcohol,* $C_{30}H_{61}OH$, is obtained in a similar manner from melissyl palmitate, the portion of beeswax sparingly soluble in hot alcohol. Melissyl alcohol occurs in *Carnauba Wax,* from *Copernicia cerifera,* Mart. (*Corypha cerifera,* Linn.) a wax characterised by its high melting-point, 176° to 194° F. (80° to 90° C.). *Yellow Beeswax* (*Cera Flava,* B.P.) and the same bleached by exposure to moisture, air, and sunlight, or *White Beeswax* (*Cera Alba,* B.P.) is prepared from the honeycomb of the hive-bee. According to Brodie it consists in the main of cerotic acid and melissyl palmitate, with about five per cent. of *ceroleine,* the substance to which the colour, odour, and tenacity of wax are due. Among the possible adulterants of wax are paraffin and *ceresine.* The latter is the purified native *ozokerite* of Galicia, a solid hydrocarbon largely used as a substitute for beeswax, especially in Russia. Both paraffin and ceresine reduce the melting-point of wax, which should not be lower than 146° F. (63·3° C.) when taken in the manner described in connection with the determination of melting-points. The quantity of paraffin and ceresine present as impurity may be determined by heating the wax first with ordinary, and afterwards with fuming, sulphuric acid, which scarcely affect these adulterants. Pure beeswax will not yield more than about three per cent. of its weight to cold rectified spirit, whereas resin, etc., would be extracted by the spirit. Solution of caustic soda extracts nothing from pure beeswax, but dissolves fatty acids, fats, resin, Japan-wax, etc., present as impurities and the alkaline fluid then yields a precipitate of acids on the addition of hydrochloric acid. Soap would be dissolved from wax on boiling the sample with water, and the aqueous fluid would yield fatty acid on adding hydrochloric acid. Flour or any starch would be detected in the cooled aqueous fluid by means of iodine. *Waxes* and *tallows* are common on leaves, fruits, and barks.

The Allyl Series of Alcohols, $C_nH_{2n-1}OH$.

Allyl alcohol, $C_3H_5{\cdot}OH$, may be obtained by heating 4 parts of glycerin with 1 of oxalic acid, the receiver being changed at 195° C., and the liquid collected till the temperature rises to 260° C. The first product is formic acid, which interacts with glycerin, forming monoformin :—

$$\underset{\text{Glycerin}}{C_3H_5(OH)_3} + \underset{\text{Formic acid}}{HCOOH} = \underset{\text{Water}}{H_2O} + \underset{\text{Monoformin}}{C_3H_5(OH)_2OCHO}$$

This, on further heating, yields allyl alcohol :—

$$C_3H_5(OH)_2OCHO = H_2O + CO_2 + C_3H_5OH.$$

By the action of the halogen acids it produces iodine, bromine, and chlorine derivatives, the OH being replaced by I, Br, or Cl ; these derivatives, when digested with potassium thiocyanate, yield allyl thiocyanate, C_3H_5CNS. This compound on distillation undergoes isomeric change, and is converted into allyl iso-thiocyanate, C_3H_5NCS, the artificial *Oil of Mustard* (identical with the chief constituent of the natural oil, *Oleum Sinapis Volatile,* B.P.). Allyl iso-thiocyanate is the substance to which mustard owes its power of inducing inflammatory action on the skin.

Mustard (*Sinapis,* B.P.) is a powdered mixture of black or, rather, reddish-brown mustard-seeds (*Sinapis Nigræ Semina,* B.P.) from *Brassica nigra,* and white mustard-seeds (*Sinapis Albæ Semina,* B.P.) from *Brassica alba.* White mustard-seed contains *sinalbin,* $C_{30}H_{42}N_2S_2O_{15}$, a glucoside which, in contact with the myrosin present in an aqueous extract of mustard, yields iso-thiocyanate of the radical *acrinyl,* a substance which forms part of the essential oil of mustard.

$$\underset{\text{Sinalbin}}{C_{30}H_{42}N_2S_2O_{15}} + \underset{\text{Water}}{H_2O} = \underset{\substack{\text{Acrinyl}\\\text{iso-thiocyanate}}}{C_7H_7ONCS} + \underset{\substack{\text{Sinapin acid}\\\text{sulphate}}}{C_{16}H_{24}O_5NHSO_4} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

Crude oil of mustard often contains *allyl cyanide,* C_3H_5CN.

Black mustard-seed contains the albumenoid ferment, *myrosin* (resembling the *emulsin* of almonds), and also potassium myronate, or *sinigrin.* The latter is the substance which, under the influence of the ferment, yields the chief part of the pungent oil of mustard.

$$\underset{\substack{\text{Potassium}\\\text{myronate}}}{KC_{10}H_{16}NS_2O_9} + \underset{\text{Water}}{H_2O} = \underset{\substack{\text{Acid potassium}\\\text{sulphate}}}{KHSO_4} + \underset{\substack{\text{Allyl}\\\text{iso-thiocyanate}}}{C_3H_5NCS} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

The quantity of myrosin in black mustard is scarcely sufficient to decompose the whole of the sinigrin, while in white mustard the quantity is more than sufficient to decompose the sinalbin. Hence the most effective mustard is a mixture of white and black. The ferments act most effectively, hence the maximum amount of pungency is produced, in mustard paste at temperatures not exceeding 100° F. (37·7° C.).

Charta Sinapis, B.P., is cartridge paper which has been coated on one side with a mixture of purified mustard and solution of indiarubber and dried.

In the old Pharmacopœia of India the seed of *Brassica juncea*, *Rai*, or *Indian Mustard Plant*, is included in addition to those of *B. alba* and *B. nigra*. It is the common mustard of warm countries. It does not differ chemically from other mustard. Allyl compounds are also met with in several other cruciferous and liliaceous plants. *Oil of garlic* owes its odour to allyl compounds; experiments carried out by F. W. Semmler show these to be allyl-propyl disulphide, and diallyl disulphide.

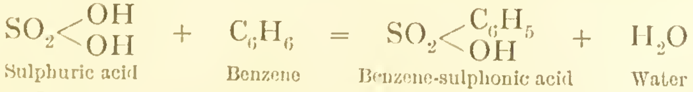
Decylene Alcohol, $C_{10}H_{19}OH$, belongs to the allyl series. Menthol (*Menthol*, B.P.), obtained from oil of peppermint, is said by some to consist wholly of this alcohol.

Sulphur Alcohols, or *Thio-alcohols*, CH_3SH, C_2H_5SH, etc., analogous to hydrosulphides, KSH, etc., are known. They were originally termed *mercaptans* (*mercurius captans*) from the readiness with which they took up mercury to form compounds such as $(C_2H_5S)_2Hg$. The vapours of thio-alcohols and many allied sulphur compounds have an extremely unpleasant smell.

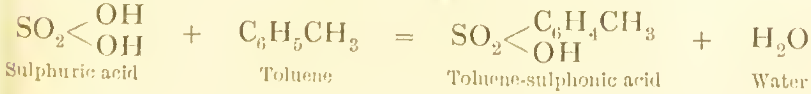
Sulphonic Acids are products of the oxidation of the sulphur alcohols just mentioned. For example :—

$$\underset{\text{Ethyl-mercaptan}}{2C_2H_5SH} + \underset{\text{Oxygen}}{3O_2} = \underset{\text{Ethyl-sulphonic acid}}{2C_2H_5{\cdot}SO_2{\cdot}OH}$$

A number of aromatic sulphonic acids may be formed by acting on hydrocarbons with sulphuric acid. Examples :—



$$\underset{\text{Sulphuric acid}}{SO_2{<}^{OH}_{OH}} + \underset{\text{Benzene}}{C_6H_6} = \underset{\text{Benzene-sulphonic acid}}{SO_2{<}^{C_6H_5}_{OH}} + \underset{\text{Water}}{H_2O}$$

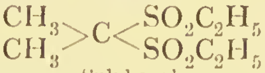


$$\underset{\text{Sulphuric acid}}{SO_2{<}^{OH}_{OH}} + \underset{\text{Toluene}}{C_6H_5CH_3} = \underset{\text{Toluene-sulphonic acid}}{SO_2{<}^{C_6H_4CH_3}_{OH}} + \underset{\text{Water}}{H_2O}$$

Sulphonic acids are isomeric with acid sulphites, the characteristic sulphonic group or radical being SO_3H, but the acid sulphites of the organic radicals are extremely unstable, the corresponding sulphonic acids very stable; the former are easily decomposed by caustic potash or soda while the latter are not attacked.

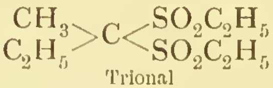
Sulphonal (B.P.), a hypnotic, is a crystalline, colourless, tasteless, odourless, substance. It is a product of the action of a permanganate solution on acetone-ethyl-mercaptol, $(CH_3)_2C\ (C_2H_5S)_2$—a liquid resulting from the interaction of hydrochloric acid, mercaptan, and acetone. Its systematic name is diethylsulphone-dimethylmethane.

Trional is diethylsulphone - methylethylmethane, and *tetronal* is diethysulphone-diethylmethane.



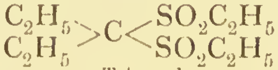
$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C<\!\begin{matrix}SO_2C_2H_5\\SO_2C_2H_5\end{matrix}$$

Sulphonal



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>C<\!\begin{matrix}SO_2C_2H_5\\SO_2C_2H_5\end{matrix}$$

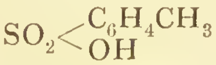
Trional



$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>C<\!\begin{matrix}SO_2C_2H_5\\SO_2C_2H_5\end{matrix}$$

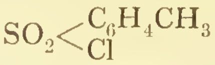
Tetronal

Saccharin (*Glusidum*, B.P.; synonym, *Glucusimide*), which is a harmless, non-alimentary, purely sweetening agent, two or three hundred times as sweet as sugar, is *benzoyl-sulphonic imide.* Fahlberg obtains it by converting toluene into toluene-sulphonic acid (above); this into a calcium salt, then into a sodium salt, and the latter into toluene-sulphonic chloride, by action of phosphorus trichloride and chlorine; the liquid orthochloride into amide by ammonium carbonate; the amide is then oxidized by potassium permanganate to potassium sulphamidobenzoate and water; hydrochloric acid then precipitating benzoyl-sulphonic imide or "saccharin" with elimination of water. "Soluble saccharin" is saccharin in which hydrogen is displaced by sodium. The following formulæ illustrate the stages of manufacture:—



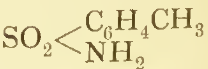
$$SO_2<\!\begin{matrix}C_6H_4CH_3\\OH\end{matrix}$$

Toluene-sulphonic acid



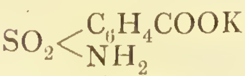
$$SO_2<\!\begin{matrix}C_6H_4CH_3\\Cl\end{matrix}$$

Toluene-sulphonic chloride



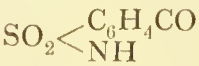
$$SO_2<\!\begin{matrix}C_6H_4CH_3\\NH_2\end{matrix}$$

Toluene-sulphonic amide



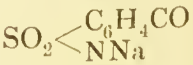
$$SO_2<\!\begin{matrix}C_6H_4COOK\\NH_2\end{matrix}$$

Potassium sulphamidobenzoate



$$SO_2<\!\begin{matrix}C_6H_4CO\\NH\end{matrix}$$

Benzoyl-sulphonic imide or "saccharin"



$$SO_2<\!\begin{matrix}C_6H_4CO\\NNa\end{matrix}$$

"Soluble saccharin"

Orthophenolsulphonic acid, $C_6H_4OH{\cdot}SO_2{\cdot}OH$, *sozolic acid*, or *aseptol*, is a non-poisonous, non-irritating antiseptic. *Diiodopara-phenolsulphonic acid*, or *sozoiodol*, $C_6H_2I_2OH{\cdot}SO_2{\cdot}OH$, has similar properties, and is used instead of iodoform.

QUESTIONS AND EXERCISES

Give an outline of the relations between alcohols and acids.—Give a general method of preparing the primary alcohols of the ethyl series.—Name the source of methyl alcohol.—What is "methylated spirit"?—Describe the mode of detecting methylated spirit in a tincture.—How can artificial ethyl alcohol be prepared?—Write a few sentences on the formation, purification, and concentration of alcohol, and explain the difference between the official varieties of alcohol, proof spirit, and absolute alcohol.—What quantity of water must be added to one gallon of alcohol 58 degrees over-proof, to convert it into proof spirit?—How far must 5 pints of alcohol of 53 degrees over-proof be diluted to become proof spirit? *Ans.*, 7 pints 13 ounces.—State the specific gravity of proof spirit.—State the proportion of alcohol commonly present in malt liquors, light wines, port and sherry, and "spirits"; and state the extent to which spirits may be diluted without "adulteration."—Enumerate the characters of alcohol.—Whence is brandy obtained, and to what are its colour and flavour due?—Give a short account of commercial amyl alcohol.—How is allyl alcohol prepared?—In what relation does allyl alcohol stand to oil of mustard and oil of garlic?

ETHERS

Ethyl Ether, or *ordinary ether*.—Into a capacious test-tube put a small quantity of alcohol (90 per cent.) and about half its volume of sulphuric acid, mix, and gently warm; the vapour of ether, recognisable by its odour, is evolved. Adapt a cork and long bent tube to the test-tube, and slowly distil over the ether into another test-tube. Half the original quantity of alcohol now placed in the generating tube will again give ether; and this operation may be repeated many times.

The preparation of ordinary ether is usually performed on a manufacturing scale. In carrying out a laboratory experiment on a somewhat larger scale than that described in the preceding paragraph (in imitation of the manufacturing process) the addition of alcohol, instead of being intermittent, is continuous, a tube conveying alcohol from a reservoir into the generating-vessel. Mix ten fluid ounces of sulphuric acid with twelve fluid ounces of alcohol (90 per cent.) in a glass retort or flask capable of containing at least two pints, and, without allowing the mixture to cool, connect the retort or flask, by means of a bent glass tube, with a Liebig's condenser, and distil with heat sufficient to maintain the liquid in brisk ebullition. (If a thermometer also be inserted in the tubulure of the retort or through the cork of the flask, the temperature may be carefully regulated—between 284° and 290° F.; 140° and 143·3° C.) As soon as the ethereal fluid begins to pass over, supply fresh alcohol in a continuous stream, and at a rate about equal to that at which the fluid distils. For this purpose use a tube furnished with a stopcock to regulate the supply, as shown above in fig. 40, connecting one end of the tube with a vessel containing the alcohol supported above the level of the retort or flask, and passing the other end through the cork of the retort or flask into the liquid. When a total of fifty fluid ounces of alcohol has been added, and forty-two fluid ounces of ether have distilled over, the process may be stopped.

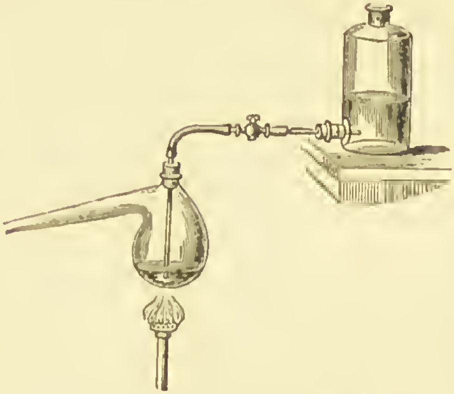


FIG. 40.—Preparation of Ether.

To partially purify the liquid, dissolve ten ounces of calcium chloride in thirteen ounces of water, add half an ounce of lime, and agitate the mixture in a bottle with the impure ether. Leave the mixture at rest for ten minutes, pour off the light supernatant fluid, and distil it gently until the specific gravity rises to 0·735. The ether and alcohol retained by the calcium chloride, and in the residue of each rectification, may be recovered by distillation and used in a subsequent operation. To imitate the process of partial purification just described, add to the small quantity of ether obtained in the previous test-tube experiment, a concentrated solution of calcium chloride and a little slaked lime; the latter absorbs any sulphurous acid that may have been produced by secondary decompositions, while the former absorbs water; on shaking the mixture and then setting aside for a minute or two, the ether will be found floating on the surface of the solution of calcium chloride.

Explanation of Process.—On mixing sulphuric acid and alcohol in equal volumes, they interact to some extent to form ethyl hydrogen sulphate (sometimes termed ethyl-sulphuric, or sulphovinic, acid):—

$$\underset{\text{Alcohol}}{C_2H_5OH} + \underset{\substack{\text{Sulphuric}\\ \text{acid}}}{H_2SO_4} = \underset{\substack{\text{Ethyl hydrogen}\\ \text{sulphate}}}{C_2H_5HSO_4} + \underset{\text{Water}}{H_2O}$$

The ethyl hydrogen sulphate interacts, on warming, with more of the alcohol to form ether and sulphuric acid:—

$$\underset{\substack{\text{Ethyl}\\ \text{alcohol}}}{C_2H_5OH} + \underset{\substack{\text{Ethyl hydrogen}\\ \text{sulphate}}}{C_2H_5HSO_4} = \underset{\substack{\text{Ether,}\\ \text{or } C_2H_5\text{—O—}C_2H_5}}{(C_2H_5)_2O} + \underset{\substack{\text{Sulphuric}\\ \text{acid}}}{H_2SO_4}$$

The water of the first reaction and the ether of the second distil over, while the sulphuric acid liberated is again attacked by alcohol and reconverted into ethyl hydrogen sulphate. So that the sulphuric acid originally employed finally remains in the retort in the form of ethyl hydrogen sulphate. The effect, however, of a small quantity of sulphuric acid in thus converting a large quantity of alcohol into ether is limited, secondary reactions occurring to some extent after a time. The official ether (*Æther*, B.P.) is "a colourless, very volatile and inflammable liquid, having a strong and characteristic odour. Sp. gr. 0·735. It contains not less than 92 per cent. by volume of ethyl oxide $(C_2H_5)_2O$."

Properties.—Pure ethyl ether is gaseous at temperatures above 95° F. (35° C.); hence the condensing tubes employed in its distillation must be kept as cool as possible. At all ordinary temperatures it rapidly volatilizes, absorbing much heat from the surface on which it is placed. A few drops evaporated from the back of the hand produce a well-marked sensation of cold; and if blown in the form of spray, the cooling effect is so rapid and intense as to produce local anæsthesia. Evaporated by aid of a current of air from the outside of a thin narrow test-tube containing water, the water may be frozen. Its vapour is very heavy, more than two and a half times as heavy as air, and nearly forty times as heavy as hydrogen, $H_2 = 2$; $C_4H_{10}O = 74$, or as 1 to 37. In a still atmosphere the vapour will flow a considerable distance along a table or floor before complete diffusion occurs, and as the vapour is highly inflammable, it is of the greatest importance to keep candle and other flames at a distance during manipulations with ether. Exposed to the action of air and light, ether undergoes some decomposition and then contains a little hydrogen peroxide.

Ether, prepared as described and distilled until the distillate has a sp. gr. of 0·735, and boiling-point not higher than 105° F. (40·5° C.), is the "Ether" of the British Pharmacopœia. It still contains about 8 per cent. of alcohol. The latter may be removed by well shaking the ether with half of its volume of water, setting aside, separating the floating ether and again shaking it with water; alcohol is thus washed out. This washed ether containing water (for water and ether are to some extent soluble the one in the other; fifty measures of pure ether agitated with an equal volume of water are reduced to forty-five measures) is placed in a retort with solid calcium chloride and a little caustic lime, and once more distilled; purified ether (*Æther Purificatus*, B.P.) results. Sp. gr. not exceeding 0·722 and not below 0·720, indicating about 99 per cent. of ethyl oxide. Shaken with about a fourth of its volume of solution of potassium iodide and a little starch mucilage, little or no blue colour is produced, indicating absence of an impurity. The exact nature of the latter is not known, but inasmuch as it develops hydrogen peroxide, the test for the latter is officially directed to be applied. "On shaking pure ether with half its bulk of a dilute solution of potassium bichromate acidulated with sulphuric acid, and setting aside, the supernatant ether should have no blue colour (absence of hydrogen peroxide)." Poleck and Thummel state that the impurity in question is vinyl alcohol.

Mixed Ethers. — That $C_2H_5 — O — C_2H_5$ represents the constitution of ether is indicated by the result of the reaction of, say, methyl alcohol on ethylsulphuric acid, a single definite substance, methyl-ethyl ether, $CH_3—O—C_2H_5$, resulting.

Ethers of various radicals, R—O—R, and several *mixed ethers*, R—O—R′, are known; also *sulphur ethers* or *thioethers*, such as $(CH_3)_2S$, $(C_2H_5)_2S$, etc.

Spiritus Ætheris, B.P., is a mixture of common ether (*Æther*, B.P.), with twice its volume of alcohol (90 per cent.).

Ethylene Sulphate, $C_2H_4SO_4$, is said to be contained in "Hoffmann's Anodyne" (*Spiritus Ætheris Compositus*, B.P.), a solution of *heavy oil of wine* in ether and alcohol. The so-called "heavy oil of wine" is obtained by digesting alcohol (90 per cent.) and sulphuric acid together, then distilling, removing any acid from the distillate by the addition of sodium bicarbonate, and adding alcohol to the ethereal liquid. The product is a mixture consisting probably of ethylene sulphate, ethyl sulphate, ether, dissolved ethylene, and other substances.

AROMATIC ALCOHOLS ($C_nH_{2n-7}OH$ *Series*)

Phenols.—These are alcohols in the sense of being hydroxyl derivatives of hydrocarbons. They possess in a slight degree the character of acids, forming compounds with metals which to some extent resemble salts. Unlike the paraffin alcohols, they do not yield aldehydes, acids, or ketones on oxidation.

Carbolic Acid

Phenol, *Phenic Alcohol*, *Phenic Acid*, or *Carbolic Acid*,* C_6H_5OH, may be prepared by heating benzene with sulphuric acid, whereby benzene-sulphonic acid, $C_6H_5HSO_3$, is obtained. This, when heated with caustic potash yields potassium-phenol or potassium carbolate, and the latter when treated with acids, yields phenol:—

$$\underset{\substack{\text{Benzene-}\\ \text{sulphonic acid}}}{C_6H_5HSO_3} + \underset{\substack{\text{Potassium}\\ \text{hydroxide}}}{3KOH} = \underset{\substack{\text{Potassium}\\ \text{carbolate}}}{C_6H_5OK} + \underset{\substack{\text{Potassium}\\ \text{sulphite}}}{K_2SO_3} + \underset{\text{Water}}{2H_2O}$$

Commercially, carbolic acid is obtained from that part of coal-tar boiling between 356° and 374° F. (180° and 190° C.). When purified, it is a colourless† crystalline solid, of melting point not lower than 102° F. (38·8° C.) (*Acidum Carbolicum*, B.P.). A crystalline, so-called hydrous, acid, C_6H_5OH,H_2O, may also be obtained.

Carbolic acid is only slightly soluble in water, but is readily dissolved by alcohol, ether, and glycerin (*Glycerinum Acidi Carbolici,* B.P.). At 60° F. (15·5° C.), 100 parts of the acid are liquefied by the addition of 5 to 10 parts of water (100 of acid and 10 of water forming *Acidum Carbolicum Liquefactum,* B.P.). At the same temperature 100 of the acid dissolve 30 to 40 of water, and are dissolved by 1800 to 1200 of water, the former of these numbers being said to be characteristic of the acicular, and the latter of the pulverulent variety of the acid. Of the small, separate crystals which are official, 1 part dissolves in 12 of water.

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* Ordinary carbolic acid is a mixture of phenol with cresol and other homologues of phenol.

† Phenol soon assumes a pink colour owing (Fabrini) to the action of hydrogen peroxide and ammonia in presence of traces of copper, iron, or lead.

At temperatures above 95° F. (35° C.) ordinary carbolic acid is an oily liquid. In odour, taste, and solubility (and in appearance when liquefied by heat or by the addition of 5 per cent. of water) carbolic acid resembles creosote, a wood-tar product for which it has been substituted. Besides phenol, coal-tar oil contains *cresol* or cresylic acid, C_7H_7OH, or $C_6H_4CH_3OH$, while wood-tar oil furnishes *guaiacol,* $C_7H_8O_2$, —also a product of the destructive distillation of guaiacum-resin, boiling-point 392°F. (200° C.)—and *creosol,* $C_8H_{10}O_2$, or $C_6H_3CH_3{\cdot}OH{\cdot}OCH_3$, the mixture constituting creosote. Certain colouring-matters may be obtained by the oxidation of carbolic acid: thus the addition of a small quantity of a solution of a hypochlorite to carbolic acid which has been mixed with ammonia or, still better, with aniline (phenyl-ammonia or phenylamine) produces a blue liquid. No very satisfactory chemical method can be found for distinguishing creosote from carbolic acid, as creosote contains phenol. Some physical differences exist: thus, carbolic acid does not affect the plane of polarization of a ray of polarized light; creosote rotates it to the left or slightly to the right according to variations in the substances present in it. Carbolic acid is either solid or may be solidified by cooling; creosote is not solidified at the low temperature attained by mixing hydrochloric acid and sodium sulphate. Creosote from coal (impure or crude carbolic acid) yields a jelly when shaken with albumen or with collodion; creosote from wood (*Creosotum,* B.P.) is scarcely affected, especially if quite free from traces of carbolic acid. Coal-creosote is soluble in solution of caustic potash and in saturated solution of ammonia (Read); wood-creosote is scarcely soluble. The coal-tar product is soluble in twenty times its volume of water, and a neutral solution of ferric chloride produces a more or less permanent green or blue colour with the liquid; wood-creosote is less soluble (*Aqua Creosoti*, U.S.P., is said to contain 1 in 129) and is not permanently coloured blue by ferric chloride. An alcoholic solution of the coal-tar creosote is coloured brown by ferric chloride, a similar solution of wood-creosote green. A dilute solution of creosote, such as creosote water, is not affected by agitation with spirit of nitrous ether while a similar solution of phenol becomes red. A few drops of spirit of nitrous ether are placed in a test-tube with about a drachm of the aqueous liquid, and an equal volume of sulphuric acid is poured down the sides of the tube. A pink or red colour results if phenol be present, especially after standing for a short time (Eykman; MacEwan). A solution of carbolic acid gives, with excess of bromine water, an insoluble white precipitate of tribromophenol, $C_6H_2Br_3OH$. This reaction is useful in quantitative determinations of carbolic acid. The determination of the amount of iodine absorbed by alkaline solutions of this and other phenols (thymol, naphthol, etc.) serves also for quantitative purposes. According to Morson pure creosote is not dissolved when mixed with an equal volume of commercial glycerin, while carbolic acid is miscible in all proportions and, if present in the creosote, will carry a considerable quantity of it into solution. Creosote is, obviously, a mixture of substances and may vary, somewhat, in composition.

Carbolic acid and alkalies yield *carbolates* or *phenates*, such as C_6H_5OK and C_6H_5ONa. Alcoholic solutions of the latter and of mercuric chloride yield yellow crystalline mercuric phenate or *phenol-mercury*, $(C_6H_5O)_2Hg$.

Carbolic acid is a powerful *antiseptic* (*ἀντί*, *anti*, against and *σήπω*, *sēpō*, to putrefy). In large doses it is poisonous, *antidotes* being a mixture of olive-oil and castor-oil, freely administered, or a mixture of slaked lime with about three times its weight of sugar rubbed together with a little water. A lozenge is official (*Trochiscus Acidi Carbolici*, B.P.). Carbolic acid is attacked by hot sulphuric acid, *sulphocarbolic* or *paraphenolsulphonic acid*, $C_6H_4(OH)SO_3H$, being formed. On diluting the product and mixing with oxides, hydroxides, or carbonates, *sulphocarbolates* are formed. The formula of *sodium sulphocarbolate* is $NaC_6H_5SO_4,2H_2O$, or $C_6H_4(OH)SO_3Na, 2H_2O$. It is obtained by heating a mixture of phenol and excess of sulphuric acid for some time to 100°-110° C. and converting the para-phenolsulphonic acid so obtained into a sodium salt, by first treating the mixture with barium carbonate, which forms insoluble barium sulphate and a solution of barium sulphocarbolate, filtering, and treating the filtrate with sodium carbonate. It forms colourless, neutral, prismatic crystals (*Sodii Sulphocarbolas*, B.P.). *Zinc Sulphocarbolate*, $[C_6H_4(OH)SO_3]_2Zn,7H_2O$ (*Zinci Sulphocarbolas*, B.P.), may be obtained by saturating sulphocarbolic acid with zinc oxide.

Trinitro-phenol, $C_6H_2(NO_2)_3OH$, is formed on slowly dropping carbolic acid into fuming nitric acid; it is the yellow dye known as *carbazotic acid*, or *picric acid*. Most of the picrates are explosive by percussion, and picric acid itself forms, when fused, the explosive known as *lyddite*.

Both carbolic acid and benzene are products obtained in the manufacture of coal-gas; hence the word *phenic* and thence *phenyl* (from *φαίνω*, *phainō*, I light, an allusion to the use of coal-gas).

Liquor Picis Carbonis, B.P., is prepared by digesting coal-tar in alcohol (90 per cent.) which has extracted the active principles of Quillaia Bark.

By heating phenol with zinc dust, benzene results,—

$$C_6H_5OH + Zn = ZnO + C_6H_6.$$

Cresol or *Tolyl Alcohol*, C_7H_7OH or $C_6H_4OH \cdot CH_3$, one of the hydroxytoluenes, is always found in crude phenol; artificially it may be made by the same general method as phenol, by acting on toluene with sulphuric acid and heating the resulting sulphonic acid, $C_6H_4(SO_3H)CH_3$, with caustic potash. With ferric chloride it gives a brown coloration. The three isomeric forms, ortho-, meta-, and para-, are known.

Benzyl Alcohol, *Phenylcarbinol*, $C_6H_5CH_2OH$, is isomeric with cresol, but has the hydroxyl group in the methane nucleus, and not in the benzene nucleus of toluene. Having the CH_2OH group, it yields on oxidation benzaldehyde, C_6H_5COH (oil of bitter almonds), and benzoic acid, C_6H_5COOH.

Dihydroxyl-Derivatives of Hydrocarbons; Dihydric or Diatomic Alcohols.

Glycols. $C_nH_{2n}(OH)_2$ series.

Glycols may be regarded as dihydroxyl-derivatives of the paraffins, the alcohols of the ethyl series being monohydroxyl-derivatives :—

$$\underset{\text{Ethane}}{C_2H_6} \qquad \underset{\text{Ethyl alcohol}}{C_2H_5OH} \qquad \underset{\text{Glycol}}{C_2H_4(OH)_2}$$

They are prepared by acting on di-iodo-derivatives of the paraffins with silver acetate, and then treating the product with caustic potash.

$$\underset{\text{Di-iodo-ethane}}{C_2H_4I_2} + \underset{\substack{\text{Silver}\\\text{acetate}}}{2CH_3COOAg} = \underset{\substack{\text{Ethylene}\\\text{acetate}}}{(CH_3COO)_2C_2H_4} + \underset{\substack{\text{Silver}\\\text{iodide}}}{2AgI}$$

$$\underset{\text{Ethylene acetate}}{(CH_3COO)_2C_2H_4} + \underset{\text{Caustic potash}}{2KHO} = \underset{\text{Glycol}}{C_2H_4(OH)_2} + \underset{\text{Potassium acetate}}{2CH_3COOK}$$

The glycols yield very interesting products on oxidation, forming two sets of acids, the lactic and the succinic series.

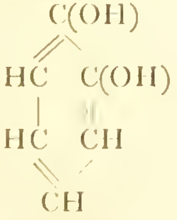
Aromatic Glycols, $C_nH_{2n-8}(OH)_2$. Dihydroxyl-derivatives of benzene.

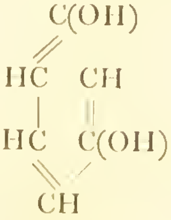
Resorcin (*Resorcinum,* U.S.P.), pyrocatechin, and hydroquinone:—

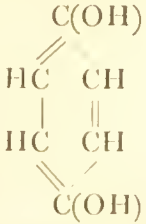
When two atoms of hydrogen in benzene are displaced by two hydroxyl groups one of the three possible isomeric compounds is *resorcin,* $C_6H_4(OH)_2$, a colourless, crystalline antiseptic having many advantages over carbolic acid in surgical operations. Its name was given in allusion to its original source, resin, and to certain similarities with orcin. It occurs in white flat prisms readily soluble in most liquids. It may be made by passing benzene vapour into hot sulphuric acid and heating the product (benzene meta-disulphonic acid, $C_6H_4(SO_2{\cdot}OH)_2$) with excess of caustic soda.

$$\underset{\substack{\text{Sodium benzene}\\\text{meta-disulphonate}}}{C_6H_4(SO_2{\cdot}ONa)_2} + \underset{\substack{\text{Caustic}\\\text{soda}}}{2NaHO} = \underset{\text{Resorcin}}{C_6H_4(OH)_2} + \underset{\substack{\text{Sodium}\\\text{sulphite}}}{2Na_2SO_3}$$

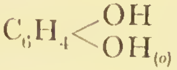
Resorcin is one of the three isomeric dihydroxy-benzenes. The chemical relationships of these isomers warrant the conclusion that the differences in their properties are due to differences in the relative positions of the two hydroxyl groups in the molecules, as represented by the following formulæ:

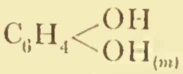

Ortho-dihydroxy-benzene (pyrocatechin)

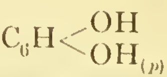

Meta-dihydroxy-benzene (resorcin)


Para-dihydroxy-benzene (hydroquinone)

These formulæ may conveniently be shortened as follows:—


$C_6H_4{<}\begin{matrix}OH\\OH_{(o)}\end{matrix}$


$C_6H_4{<}\begin{matrix}OH\\OH_{(m)}\end{matrix}$


$C_6H{<}\begin{matrix}OH\\OH_{(p)}\end{matrix}$

Among the benzene or aromatic compounds there are many similar sets of three isomeric di-substitution derivatives (three xylenes, three phthalic acids, etc.), the occurrence of which is in complete agreement with the "benzene ring" hypothesis of Kekulé as to the constitution of benzene compounds.

Orcin, or *dihydroxy-toluene*, $C_6H_3(OH)_2CH_3$, is found in lichens.

Saligenol or *saligenin* is a *hydroxy-benzyl alcohol*, salicyl alcohol, $C_6H_4OH{\cdot}CH_2OH$. It is obtained from the salicin of willow bark. Having a hydroxyl group in the methane nucleus as well as in the benzene nucleus, salicylaldehyde, $C_6H_4OH{\cdot}COH$, and salicylic acid, $C_6H_4OH{\cdot}COOH$, are formed on oxidation.

Trihydroxyl-Derivatives of Hydrocarbons; Trihydric or Triatomic Alcohols.

Glycerol series, $C_nH_{2n-1}(OH)_3$. The only member of this series which we shall consider here is:—

Glycerin

Glycerol,* propenyl alcohol, glycerin, $C_3H_5(OH)_3$.—The propenyl or glyceryl radical of glycerin in combination chiefly with the acid radicals of oleic, palmitic, and stearic acids, forms most of the solid fats and fixed, *i.e.*, non-volatile oils. When these latter substances are heated with metallic hydroxides, interaction occurs, oleate, palmitate, or stearate of the metal is formed, and glycerin (glyceryl hydroxide) is set free. Hence glycerin is a by-product in the manufacture of soap, hard candles, and lead plaster. The fats are also decomposed when exposed to the action of steam at from 500° to 600° F. (260° to about 315° C.) glycerin and oleic, palmitic, or stearic acid being formed.

Properties.—Glycerin is a viscid liquid of sp. gr. 1·28 (1·260, B.P., 1898); it has a sweet taste, and is soluble in water or alcohol in all proportions. It has remarkable powers as a solvent, is a valuable *antiseptic* even when diluted with 10 parts of water, and is useful as an emollient. Under reduced pressure it may be distilled unchanged, but at ordinary atmospheric pressure it undergoes partial decomposition on distillation. In a shallow open vessel heat readily vaporizes it if a little water be present. From damp air glycerin absorbs moisture slowly, but in considerable proportions. Perfectly pure and anhydrous glycerin, at a few degrees below the freezing point of water, sometimes solidifies to a mass of crystals.

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* It will be noticed that one of the names of each alcohol has the termination *-ol*, carbinol, glycol, glycerol, saligenol, pyrogallol.

Tests.—Heat one or two drops of glycerin in a test-tube, alone or with concentrated sulphuric acid, acid potassium sulphate, or other salt powerfully absorbent of water; vapours of acrylaldehyde or acrolein (from *acer*, sharp, and *oleum*, oil) are evolved, recognisable by their powerfully irritating effects on the eyes and respiratory passages. If the glycerin be in solution, the latter must be evaporated to as small a volume as possible before the test is applied.

$$\underset{\text{Glycerin}}{C_3H_5(OH)_3} = \underset{\text{Water}}{2H_2O} + \underset{\text{Acrylaldehyde}}{CH_2:CH \cdot COH}$$

To some dilute solution of borax, reddened by the addition of phenol-phthalein, add a few drops of a solution (neutralized, if necessary) suspected to contain glycerin; if any is present, the colour will be discharged owing to the liberation of free boric acid, but will re-appear on heating the solution; this reaction is also given by other polyhydroxy alcohols, such as mannite or glucose.

Add a few drops of the fluid suspected to contain the glycerin to a small quantity of powdered borax; stir well together; dip the looped end of a platinum wire into the mixture, and heat in the Bunsen flame; a deep green colour is produced (Senier and Lowe).

The glycerin liberates boric acid, which colours the flame (*see* p. 366). Ammonium salts, which similarly affect borax, must first be got rid of by boiling with solution of sodium carbonate. Acids must be neutralized. Liquids containing much indefinite organic matter must sometimes be evaporated to dryness, the residue extracted with alcohol, and the alcoholic extract tested for glycerin. To detect traces, liquids must be concentrated.

Glycerin, by action of concentrated nitric acid, yields *trinitrine, nitroglycerin,* or *glyceryl nitrate,* $C_3H_5(NO_3)_3$. It is highly explosive, a very small quantity being liable to explode during preparation, and with great violence. 75 parts of nitroglycerin absorbed by 25 of porous silica, yield a pasty mass, more convenient to handle than nitroglycerin itself, which is used for blasting, under the name of *dynamite.* Tablets of chocolate, weighing 5 grains, and containing $\frac{1}{100}$ grain of nitroglycerin, constitute the *Tabellæ Trinitrini,* B.P. A 1 per cent. solution in alcohol (90 per cent.) is the *Liquor Trinitrini,* B.P. Its sp. gr. is 0·840.

Besides glycerin itself (*Glycerinum,* B.P.), there are several official preparations of glycerin—solutions of carbolic and tannic acids and of borax in glycerin, and also a species of mucilage of starch in glycerin—*Glycerinum Acidi Borici, Glycerinum Acidi Carbolici, Glycerinum Acidi Tannici, Glycerinum Aluminis, Glycerinum Amyli, Glycerinum Boracis, Glycerinum Pepsini, Glycerinum Plumbi Subacetatis,* and *Glycerinum Tragacanthæ.*

Fats and Oils

Processes of extraction.—Fixed oils and fats are extracted from animal and vegetable substances by pressure or straining, with or without the aid of heat, or by digestion in solvents, as ether, etc., and evaporation of the solvent.

Constitution and general relations.—Fixed oils and fats are ethereal salts or esters, and the metallic salts (soaps) obtained from them by the action of metallic hydroxides (by saponification) are quite comparable with the salts of other organic acids. Just as potassium acetate, $KC_2H_3O_2$, is a compound of potassium (K) with the acid radical of the acetates, ($C_2H_3O_2$), so soft soap is a compound of potassium with the acid radical of the oleates, ($C_{18}H_{33}O_2$), and hence is chemically termed potassium oleate, $KC_{18}H_{33}O_2$. Olive oil (*Oleum Olivæ,* B.P.), from which soap is officially prepared, is mainly oleate of the trivalent radical *glyceryl,* (C_3H_5); the formula of this oleate is $C_3H_5(C_{18}H_{33}O_2)_3$, and its name *oleine.* The formation of a soap, therefore, on bringing together oil and a moist oxide or hydroxide, is an ordinary case of double decomposition, as seen already in connection with lead plaster (p. 252), or as illustrated in the following equation representing the formation of common hard soap:—

$$\underset{\substack{\text{Sodium}\\\text{hydroxide}\\\text{(caustic soda)}}}{3NaOH} + \underset{\substack{\text{Glyceryl oleate}\\\text{(vegetable oil)}}}{C_3H_5(C_{18}H_{33}O_2)_3} = \underset{\substack{\text{Sodium oleate}\\\text{(hard soap)}}}{3NaC_{18}H_{33}O_2} + \underset{\substack{\text{Glyceryl}\\\text{hydroxide}\\\text{(glycerin)}}}{C_3H_5(OH)_3}$$

Berthelot has succeeded in preparing oil artificially from hydrogen oleate, or oleic acid, $HC_{18}H_{33}O_2$, and glycerin; and it is said to be identical with the pure oleine of olive oil and of other fixed oils.

Olive oil is liable to contain cotton-seed oil, itself a good oil, but cheaper than olive oil; it may be detected by Bechi's test. The following are the official directions for carrying out the test:—If 10 c.c. of the oil be shaken with 2 c.c. of a reagent prepared by dissolving 1 gramme of silver nitrate in 100 c.c. of absolute alcohol, with the addition of 20 c.c. of ether and one drop of nitric acid, no blackening should occur when the mixture is heated on a water-bath for ten minutes.

Hard fats chiefly consist of *stearine*—that is, of glyceryl tristearate, $C_3H_5(C_{18}H_{35}O_2)_3$. Mr Wilson, of Price's Candle Company, obtained stearic and oleic acids and glycerin by simply passing steam, heated to 500° or 600° F. (260° or 315·5° C.), through melted fat. Both the glycerin and the fat-acids distil over in the current of steam, the glycerin dissolving in the condensed water, the fat-acids floating on the aqueous liquid. From glyceryl oleate and steam there result hydrogen oleate (oleic acid) and glyceryl hydroxide (glycerin).* The oleic acid (*Acidum Oleicum*, B.P.) is separated by cooling and pressing the mixture. It is a straw-coloured liquid, nearly odourless and tasteless, and with not more than a very faint acid reaction. Unduly exposed to air, it becomes brown and decidedly acid: Sp. gr. 0·890 to 0·910. It is insoluble in water, but readily soluble in alcohol, chloroform, and ether. At 40° to 41° F. (4·5° to 5° C.) it becomes semi-solid, melting again at 56° to 60° F. (13·3° to 15·5° C.). It should be completely saponified when warmed with potassium carbonate; and an aqueous solution of the resulting salt, neutralized by means of acetic acid and treated with lead acetate, should yield a precipitate which, after washing with boiling water, is almost entirely soluble in ether, showing the absence of any important quantity of stearic and palmitic acids, lead stearate and palmitate being insoluble in ether.

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* Any such decomposition of water and fixation of its elements, whether direct as above, or indirect through the intermediate agency of saponification, is termed *hydrolysis* (ὕδωρ, *hudōr*, water, λύω, *lūo*, I decompose). The fixation of water without such actual separation of its elements from each other is termed *hydration*.

In a mixture of oils or fats and free fatty acids, the latter may be determined by taking advantage of their solubility in alcohol (90 per cent.), and the formation of a neutral soap on shaking the alcoholic solution with caustic soda, phenol-phthalein being used as indicator. (*See* the section on the use of standard sodium hydroxide solution in volumetric analysis.)

The author found, *Pharmaceutical Journal*, March 1863, that oleic acid readily combines with alkaloids and most of the metallic oxides or hydroxides forming *oleates* which are soluble in fats. In this way active medicines may be administered internally in conjunction with oils, or externally in the form of ointments (*Hydrargyri Oleas*, B.P., *Unguentum Hydrargyri Oleatis*, B.P., and *Unguentum Zinci Oleatis*, B.P.; *Oleatum Veratrinæ*, U.S.P.). Tichborne considers the formula of mercuric oleate to be $Hg(C_{18}H_{33}O_2)_2,H_2O$.

Some fats, such as "suint" from sheep's wool, and the unctuous matter from bristles, feathers, horn, and hair generally, yield by saponification, etc., fatty acids and, instead of glycerin, *cholesterin*, $C_{27}H_{45}OH$, a crystalline monatomic alcohol. The "lanoline" of pharmacy is cholesterin fat which has absorbed a large volume of water.

Wool Fat (*Adeps Lanæ*, B.P.) is "the purified cholesterin-fat of sheep's wool." It is "a yellowish, tenacious, unctuous substance; almost inodorous; melting-point varies from 104° to 112° F. (40° to 44·4° C.); readily soluble in ether or in chloroform, sparingly soluble in alcohol (90 per cent.). 1 gramme should dissolve almost completely in 75 cubic centimetres of boiling alcohol (90 per cent.), the greater part separating in flocks on cooling. When incinerated with free access of air, it leaves not more than 0·3 per cent. of ash, which should not be alkaline to litmus. 10 grammes dissolved in 25 cubic centimetres of ether, two drops of solution of phenol-phthalein being added, should not require more than 0·1 cubic centimetre of volumetric solution of sodium hydroxide to produce a permanent red coloration (limit of acidity). Its solution in chloroform poured gently over the surface of sulphuric acid acquires a purple-red colour. Heated with solution of sodium hydroxide, no ammoniacal odour should be evolved (absence of nitrogenous animal matter)."

Hydrous Wool Fat (*Adeps Lanæ Hydrosus*, B.P.) is an intimate mixture of 7 parts of wool fat with 3 of water. It is commonly known as "Lanoline." It is "yellowish white; free from rancid odour. When heated it separates into an upper oily, and a lower aqueous, layer. 10 grammes heated on a water-bath, with stirring, until the weight is constant, should yield not less than 7 grammes of residue, which should answer to the tests for Wool Fat."

Soaps

Olive oil boiled with solution of caustic potash yields potassium soap, or *soft soap* (*Sapo Mollis*, B.P.); with caustic soda, sodium soap, or *hard soap* (*Sapo Durus*, B.P.), or *white Castile soap*, as distinguished from the variety of hard Castile, or Marseilles soap, which is "mottled" by iron soap; mixed with ammonia and almond oil, an ammonium soap (*Linimentum Ammoniæ*, B.P.), and with lime-water, calcium soap (*Linimentum Calcis*, B.P.),—all containing oleates, chiefly, of the respective metallic radicals. Their mode of formation is indicated in the equation on p. 509. The alkali-metal soaps are soluble in alcohol, the others insoluble. A green soap, much used on the continent of Europe, and, indeed, official in Germany (formerly as *Sapo Viridis*, now as *Sapo Kalinus Venalis*), is made by adding indigo to ordinary soft soap; the yellow colour of the soap yielding with the indigo a greenish compound. The official characters of Hard Soap are:—"greyish-white, dry, inodorous; becomes horny and pulverizable when kept in dry warm air. Easily moulded when heated. Soluble in alcohol (90 per cent.), especially on warming. Soluble in 20 parts of cold water, and in 1½ parts of hot water. It does not impart a greasy stain to white unglazed paper. Incinerated it yields an ash which does not deliquesce." And of Soft Soap:—"yellowish-white, sometimes yellowish-green, almost inodorous, of an unctuous consistence. Readily soluble in alcohol (90 per cent.), especially on warming, the liquid, on filtration, yielding not more than 3 per cent. of residue. It does not impart an oily stain to paper. Incinerated it yields an ash which is very deliquescent, and which should afford no reaction with the tests for copper." Curd Soap (*Sapo Animalis,* B.P.) is a "soap made with sodium hydroxide and a purified animal fat consisting principally of stearin." It will, of course, chiefly contain sodium stearate. In pharmacy it is often advantageously employed instead of the "hard soap."

The hard soap met with in commerce is made from all varieties of oil, the commoner kinds being simply the product of the evaporated mixture of oil and caustic soda, while the better sorts have been separated from alkaline impurities and from the glycerin produced on boiling the oil with caustic soda lye, by the addition of common salt, or of excess of lye, to the liquors, which causes the precipitation of the pure soap as a curd. Potash soap is not so readily precipitable by salt; moreover, some soda soap results. Saponification on the small scale is much facilitated by first well mixing the oil with 5 per cent. of sulphuric acid, and letting this mixture stand for twenty-four hours. The dark product is then readily soluble when boiled with caustic soda, and the clear liquid yields a crust of white soap on cooling. If required quite free from alkali, the resulting soap is boiled with water until dissolved, salt is added, and the whole cooled. A cake of pure soap results.

Soap prepared for the use of Mahommedans and Hindoos should not contain hog fat or its oleine or stearine. As regards the official *Sapo Durus,* the Gov. Ind. Edit. 1901, of the B.P. Add. 1900, has the following paragraph. "In India, Arachis Oil or Sesame Oil, but no other oil or fat, may be employed instead of Olive Oil in making the official Hard Soap." *See* also under "Lard" and "Benzoated Lard."

The cleansing action of soap is really the cleansing action of a dilute solution of alkali, a small quantity of soap interacting with a large quantity of water to form acid stearates and palmitates, and even acid oleates after a time, which separate from the solution, and free alkali, which remains in solution.

Yellow soap is a common, cheap soap, containing a good deal of resin soap, resin consisting chiefly of acids—pinic, sylvic, pimaric, etc.—which readily interact with alkalies to form true soaps.

Saponification.—This term is now extended in chemistry so as to include any process analogous to the foregoing,—any reaction in which an alkali decomposes an ethereal salt or alkyl salt (ester).

Solid Fats

1. *Lard* (*Adeps*, B.P.) is the purified internal fat of the abdomen of the hog—the perfectly fresh *omentum* or *flare*, freely exposed to the air to dissipate animal odour, rubbed to break up the membranous vesicles, melted at about 130° F. (54·4° C.), and filtered through paper or flannel. 2. *Benzoated Lard* (*Adeps Benzoatus*, B.P.) is lard heated over a water-bath with benzoin (fifty parts to one and a half), which communicates an agreeable odour and prevents or retards rancidity. Purified lard is a mixture of oleine and stearine. The oleine removed by pressure (*lard oil*) leaves *Adeps Induratus*, B.P., 1898, and B.P. Add. 1900, an article which, however, being derived from the hog, is omitted from the special "Government of India Edition," 1901, of the Ind. and Col. Add. 1900, its place being taken by Prepared Suet and the place of Benzoated Lard by Benzoated Suet (*Sevum Benzoatum*, Gov. Ind. Edit. 1901, of B.P., Add. 1900) obtained by the official process for benzoating lard. *Margarine*, formerly supposed to be a constituent of lard and other soft fats, is now regarded as a mere mixture of *palmitine* (the chief fat of palm-oil) and stearine. 3. *Suet*, the internal fat of the abdomen of the sheep, purified by melting and straining, forms the official *Prepared Suet* (*Sevum Præparatum*, B.P.); it is almost exclusively composed of stearine, or glyceryl stearate, $C_3H_5(C_{18}H_{35}O_2)_3$. *Tallow* is chiefly mutton-fat, and beef-fat, but may contain other animal fats; some vegetable fats also are termed tallow. 4. Expressed oil of *Nutmeg*, commonly but erroneously termed *Oil of Mace*, is a mixture of a little volatile oil with much yellow and white fat; the latter is *myristin* or glyceryl myristate, $C_3H_5(C_{14}H_{27}O_2)_3$. 5. Oil of *Theobroma*, or *Cacao butter* (*Oleum Theobromatis*, B.P.), chiefly stearine, but with one higher and some lower homologues (Heintz), is a solid fat pressed from *cocoa nibs*, the roasted and broken seeds of the *Theobroma Cacao*. The seeds contain from one-half to two-thirds of this fat. [Cocoa is too rich for use as food, hence it is diluted with farina (affording "*cheap cocoa*") or sugar (affording *chocolate*) or has a portion of its fat extracted, while its solublity is, in certain brands, usefully increased by a process which results in a slight addition to the potassium salts of its ash, chiefly to the potassium phosphate.] 6. *Cocoa-*

nut oil or butter,) a soft fat contained in the edible portion of the nut of *Cocos nucifera*, or cocoa-nut of the shops, is a mixture containing glyceryl compounds of six acid radicals—namely, those of caproic ($C_6H_{11}O_2$), caprylic ($C_8H_{15}O_2$), rutic ($C_{10}H_{19}O_2$), lauric ($C_{12}H_{23}O_2$), myristic ($C_{14}H_{27}O_2$), and palmitic ($C_{16}H_{31}O_2$) acids—which, like some acid radicals from resin, when united with sodium, form a soap differing from ordinary hard soap (sodium oleate) by being tolerably soluble in a solution of sodium chloride; hence the use of cocoa-nut oil and resin in making *marine soap*, a soap which for the reason just indicated, readily yields a lather in sea-water. 7. *Kokum Butter*, Garcinia Oil, or Concrete Oil of Mangosteen, a whitish or yellowish-white fat obtained from the seeds of *Garcinia Indica* or *G. purpurea*, is composed of stearine, myristicine, and oleine. It is recognised in the old Pharmacopœia of India (*Garciniæ purpureæ Oleum*).

Butter commonly yields 87½ per cent. of insoluble fat acids on saponification and decomposition of the soap by acid. Other animal fats, with which butter is likely to be adulterated, yield about 95½. Hence the percentage of fat acids, and, especially, volatile acids, insoluble acids, and soluble acids, yielded by a suspected sample of butter, indicates purity or the opposite. Occasionally, however, a sample of genuine butter may not conform to the figures, hence they cannot be relied on to show the exact extent of sophistication.

Fixed Oils

Fixed and Volatile oils are naturally distinguished by their behaviour when heated; they also differ in their chemical nature, a fixed oil being, as already stated, an ethereal salt, while a volatile oil is usually a hydrocarbon of some kind, mixed with a comparatively small proportion of a substance—containing oxygen as well as carbon and hydrogen—to which the odour of the oil is largely due. Substances of the latter kind are now articles of trade under the name of "concentrated essential oils."

Drying and Non-drying Oils.—Among fixed oils, most of which are glyceryl oleate with a little palmitate and stearate, a few such as—1. *Linseed* oil (*Oleum Lini*, B.P., contained in *Linum*, B.P., which, when reduced to a coarse powder, is crushed linseed, *Linum Contusum*, B.P.), and 2. *Cod-liver* oil (*Oleum Morrhuæ*, B.P.), and, to some extent, *castor* and *croton* oils, are known as *drying oils,* from the readiness with which they absorb oxygen and become hardened to a resin. Linseed commonly contains 37 or 38 per cent. of oil; 25 to 27 per cent. is obtained by submitting the ground seeds to hydraulic pressure, 10 to 12 per cent. remaining in the residual *oil-cake. Boiled oil* is linseed oil which has been boiled with lead oxide. This treatment increases the already great tendency of linseed oil to resinify, forming *linoxyn* on exposure to air. The drying oils appear to contain linoleine, an oily substance distinct from oleine. Cod-liver oil contains an unimportant trace of iodine, 1 in one or two million parts, according to Stanford; a little choline is found also, and other bases, Gautier and Mourgues having isolated *aselline,* $C_{25}H_{32}N_4$, and *morrhuine,* $C_{19}H_{27}N_3$, besides butyl-, amyl-, and hexyl-amines and dihydro-lutidine. Among the *non-drying oils* are the following:—3. *Almond* oil (*Oleum Amygdalæ,* B.P.), yielded both by the bitter (*Amygdala Amara,* B.P.) and the sweet seed (*Amygdala Dulcis,* B.P.), to the extent of 45 and 50 per cent. respectively. 4. *Lycopodium,* a yellow powder composed of the spores of the common Club-Moss (*Lycopodium clavatum*), contains a large proportion of a very fluid fixed oil; also an alkaloid (Bödeker), *lycopodine,* $C_{32}H_{52}N_2O_3$. 5. Oil of *male fern* (*Filix Mas,* B.P.), a vermifuge obtained by exhausting the rhizome with ether and removing the ether by evaporation—a dark-coloured oil containing a little volatile oil and resin, and officially termed an extract (*Extractum Filicis Liquidum,* B.P.). Its active constituent appears to be *filmaron,* $C_{47}H_{54}O_{16}$, a bright yellowish-brown powder, insoluble or sparingly soluble in water and alcohol, but easily soluble in ether, acetone, etc. By certain decompositions filmaron yields *filicic acid,* $C_{14}H_{16}O_5$. The extract also contains flavaspidic acid, aspidinol, and other substances. 6. Fixed oil of *mustard,* a bland, inodorous, yellow or amber oil, yielding by saponification and action of sulphuric acid, glycerin, oleic acid, and *erucic acid,* $HC_{22}H_{41}O_2$ (Darby). 7. *Arachis* oil (*Oleum Arachis,* B.P. Add. 1900, and P.I.) is found to the extent of 40 or 50 per cent. in the seeds of the *Arachis hypogæa,* the Pea-nut, Ground-nut, or Earth-nut (so-called because the pod of the herb by the growth of its stalk downwards is forced beneath the surface of the ground and there ripens). It is chiefly oleine, but contains hypogæine, palmitine, and arachine. The oil is largely used in India in place of olive oil, and is becoming much employed in Europe, especially for soap-making. 8. *Olive* oil (*Oleum Olivæ,* B.P.), already noticed. 9. *Shark-liver* oil, from *Squalus carcharias* (*Oleum Squalæ,* P.I.), is used as a substitute for cod-liver oil in India. 10. *Croton* oil (*Oleum Crotonis,* B.P.). Geuther states that no such acid as crotonic is obtainable from croton oil, but acetic, butyric, valerianic, and higher members of the oleic series, together with *tiglic acid,* $HC_5H_7O_2$. H. Senier states that alcohol separates croton oil into a soluble oil containing the powerful vesicating principle of croton oil and an insoluble non-vesicating but powerfully purgative principle. Kobert states that free crotonoleic acid is both the vesicant and the purgative. 11. *Sesamé* oil (*Oleum Sesami,* B.P. Add. 1900; Gingelly, Teal, or Benne Oil) from the seeds of *Sesamum indicum,* is also largely used in Europe. It has most of the characters of the best olive oil. It may be detected in olive oil by well shaking the sample with a solution of pyrogallol in concentrated hydrochloric acid, and separating and boiling the acid liquid, a purplish colour resulting if sesamé oil be present. 12. *Gynocardia* oil (*Oleum Gynocardiæ,* B.P. Add. 1900) or *Chaulmoogra* oil, from the seeds of *Gynocardia odorata* (*Chaulmugra,* P.I.). It consists of gynocardic, palmitic, hypogæic, and cocinic glycerides, with some gynocardic and palmitic acids (Moss). 13. *Castor* oil (*Oleum Ricini,* B.P.) is chiefly *glyceryl ricinoleate,* $C_3H_5(C_{18}H_{33}O_3)_3$, or ricinoleine, a slightly oxidized oleine, soluble, unlike most fixed oils, in alcohol and in glacial acetic acid. Castor-oil seeds were stated, by Tuson, to contain an alkaloid, *ricinine,* to which Beck gave the formula $C_{24}H_{32}N_7O_3$. Soave holds that ricinine is not an alkaloid and that its formula is $C_{17}H_{18}N_4O_4$. It possesses no purgative property. Castor-oil seeds also contain an albumose, *ricin,* resembling, physiologically, but not quite chemically, the *abrin* of jequirity.

Trihydric Alcohols of the $C_nH_{2n-9}(OH)_3$ series.

Pyrogallol or *Pyrogallic acid.* — Trihydroxybenzene, $C_6H_3(OH)_3$. (*See* p. 394.)

Polyhydric alcohols. *Erythrite* or *Lichen Sugar,* $C_4H_6(OH)_4$, found in *Protococcus vulgaris, Roccella tinctoria,* and *R. fuci-*

formis, is one of the few known *tetrahydric* alcohols. *Quercite*, the sugar of acorns, is *pentahydric*; *Mannite* is *hexahydric*. *Sorbite*, which is also hexahydric, occurs in the fruits of the order *Rosaceæ*.

Mannite, $C_6H_8(OH)_6$.—Boil manna with 15 or 16 parts of alcohol (90 per cent.), filter, and set aside; mannite separates in colourless shining crystals or acicular masses, to the extent of from 60 to 80 per cent. of the manna. It is closely related to the ordinary sugars, fructose (levulose) yielding mannite by the action of nascent hydrogen (sodium amalgam):—

$$\underset{\text{Fructose}}{C_6H_{12}O_6} + \underset{\text{Hydrogen}}{2H} = \underset{\text{Mannite}}{C_6H_{14}O_6}$$

Mannite or *mannitol* does not undergo fermentation in contact with yeast. With nitric acid it forms explosive *nitromannite*, $C_6H_8(NO_3)_6$.

Manna is a concrete saccharine exudation obtained by making transverse incisions in the stems of cultivated trees of *Fraxinus Ornus*. It occurs in stalactitic pieces, varying in length and thickness, flattened or somewhat concave and of a pale yellowish-brown colour on their inner surface, and nearly white externally. This manna, which is known as flake manna, is crisp, brittle, porous, crystalline in structure, and readily soluble in about six parts of water. Odour faint, resembling honey; taste sweet and honey-like, combined with a slight acridity and bitterness. It contains about 10 per cent. of moisture. Mannite is also met with in celery, onions, asparagus, certain fungi and sea-weeds; it occurs in the exudations of apple-trees and pear-trees, and is produced during the viscous fermentation of sugar. When oxidized it yields first the sugar termed *mannose*, $CH_2OH(CHOH)_4COH$, then some *mannonic acid*, $CH_2OH(CHOH)_4COOH$, and finally *saccharic acid*, $(CHOH)_4(COOH)_2$.

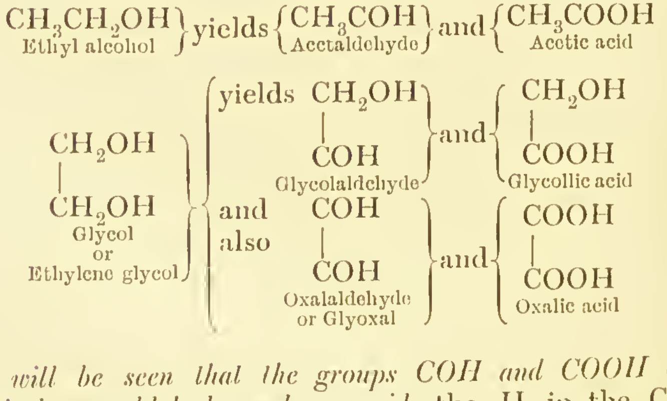
Dulcite, isomeric with mannite, is formed by the action of sodium amalgam on galactose (from milk sugar). It differs from mannite by yielding mucic acid, $(CHOH)_4(COOH)_2$, isomeric with saccharic acid, when oxidized with nitric acid.

QUESTIONS AND EXERCISES

Describe the process for the preparation of ether, giving equations.—How is commercial ether purified?—How is phenol artificially and commercially prepared?—How would you distinguish carbolic acid from creosote?—Give the formulæ and systematic names for picric acid, sodium carbolate, and resorcin.—Give names for the substances having the formulæ $C_6H_4OH{\cdot}CH_3$ and $C_6H_5CH_2OH$.—What are glycols and how are they prepared?—Give formula and mention the chief properties of glycerin.—What is the specific gravity of glycerin?—By what tests is glycerin recognised?—Enumerate some official preparations in which glycerin is employed.—Give a sketch of the general chemistry of fixed oils, fats, and soaps.—What is the difference between hard and soft soap?—Which soaps are official?—Name the source of lard. How is "*Adeps*, B.P.," obtained?—Mention the chief constituents of suet.—Whence is cacao-butter obtained?—Why is *marine soap* so called, and from what fatty matter is it almost exclusively prepared?—What do you understand by *drying* and *non-drying* oils?—In what respect does castor oil differ from other oils?—How is oil of male fern (*Extractum Filicis Liquidum*, B.P.) prepared?—Classify pyrogallol (*Pyrogallic acid*), erythrite, mannite, and dulcite.—Describe the source and characters of manna.

ALDEHYDES AND ACIDS

Aldehydes and acids may be formed by the oxidation of the primary alcohols, glycols, etc. Monohydric alcohols, having only one hydroxyl (OH) group, form monobasic acids, dihydric alcohols (glycols) having two hydroxyl groups, yield monobasic and dibasic acids; and so on. Thus:—



$$\left.\underset{\text{Ethyl alcohol}}{CH_3CH_2OH}\right\}\text{yields}\left\{\underset{\text{Acetaldehyde}}{CH_3COH}\right\}\text{and}\left\{\underset{\text{Acetic acid}}{CH_3COOH}\right.$$

$$\left.\underset{\substack{\text{Glycol}\\ \text{or}\\ \text{Ethylene glycol}}}{\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix}}\right\}\left\{\begin{matrix}\text{yields}\left.\underset{\text{Glycolaldehyde}}{\begin{matrix}CH_2OH\\ |\\ COH\end{matrix}}\right\}\text{and}\left\{\underset{\text{Glycollic acid}}{\begin{matrix}CH_2OH\\ |\\ COOH\end{matrix}}\right.\\ \text{and also}\left.\underset{\substack{\text{Oxalaldehyde}\\ \text{or Glyoxal}}}{\begin{matrix}COH\\ |\\ COH\end{matrix}}\right\}\text{and}\left\{\underset{\text{Oxalic acid}}{\begin{matrix}COOH\\ |\\ COOH\end{matrix}}\right.\end{matrix}\right.$$

It will be seen that the groups COH and COOH denote respectively an aldehyde and an acid, the H in the COOH group being replaceable by a metal, as in the case of $CH_3{\cdot}CO{\cdot}ONa$ (sodium acetate).

Acids may also be obtained by acting on the *nitriles* * (or cyanides of the hydrocarbon radicals) with hydrochloric acid and water. Thus :—

$$\underset{\text{Acetonitrile}}{CH_3CN} + \underset{\text{Water}}{2H_2O} + \underset{\substack{\text{Hydrochloric}\\\text{acid}}}{HCl} = \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\substack{\text{Ammonium}\\\text{chloride}}}{NH_4Cl}$$

Many aldehydes and acids occur in nature ; for example, oil of meadow-sweet (salicylaldehyde), oil of bitter almonds (benzaldehyde), tartaric acid, citric acid, etc.

General Reactions.—Aldehydes form crystalline compounds with acid potassium sulphite ; by oxidation they yield acids, and by the reducing action of nascent hydrogen they yield alcohols ; while acids yield aldehydes and then alcohols by reduction with nascent hydrogen. With oxides, hydroxides, carbonates, and sometimes with metals, acids form metallic derivatives (salts). With the alcohols, acids yield alkyl † or ethereal salts, as, for instance, acetic ether. By the action of the chloride, iodide, or bromide of phosphorus their hydroxyl group is replaced by chlorine, iodine, or bromine :—

$$\underset{\substack{\text{Acetic}\\\text{acid}}}{3CH_3COOH} + \underset{\substack{\text{Phosphorus}\\\text{trichloride}}}{PCl_3} = \underset{\substack{\text{Acetyl}\\\text{chloride}}}{3CH_3CO{\cdot}Cl} + \underset{\substack{\text{Phosphorous}\\\text{acid}}}{PO_3H_3}$$

Like inorganic acids, they form anhydrides by the elimination of water :—

$$\underset{\text{Acetic acid}}{2CH_3COOH} - \underset{\text{Water}}{H_2O} = \underset{\text{Acetic anhydride}}{\left.\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\right\}O}$$

---

* The nitriles may be prepared by the interaction of the halogen derivatives of the hydrocarbons with potassium cyanide :—

$$\underset{\substack{\text{Methyl}\\\text{chloride}}}{CH_3Cl} + \underset{\substack{\text{Potassium}\\\text{cyanide}}}{KCN} = \underset{\substack{\text{Methyl cyanide}\\\text{or acetonitrile}}}{CH_3CN} + \underset{\substack{\text{Potassium}\\\text{chloride}}}{KCl}$$

The reactions of nitriles indicate that the hydrocarbon radical is united to the carbon of the cyanogen group. In the isomeric substances called *isonitriles* or *carbamines* (obtained by the interaction of the halogen derivatives of the hydrocarbons with silver cyanide) the hydrocarbon radical appears to be united to the nitrogen of the cyanogen group.

† *Alkyl Salts.* *Alkyl*, from the Arabic article *al*, the, as in alkali, alcohol, etc., and the termination common to the names of such radicals as ethyl, amyl, and phenyl, and as seen in methyl, the prototype of such names. In Germany the word *ester* (*see* p. 462), a mere variation of the word *ether*, is similarly employed. In the scientific chemistry of both countries it is thus sought to restrict the name *ethers* to the organic radical oxides, as common ether, $(C_2H_5)_2O$ (*Æther*, B.P.).

The important aldehydes and acids will now be mentioned.

The Acetic Series of Monobasic Acids, $C_nH_{2n+1}CO \cdot OH$.

These acids are formed by the two general methods given, namely, from primary alcohols of the ethyl series and from cyanides of the paraffin hydrocarbon radicals.

Formic Acid, $H \cdot COOH$. *See* p. 370. Formaldehyde, $H \cdot COH$, is obtained by passing a mixture of methyl alcohol vapour and air over a heated spiral of metallic copper. At ordinary temperatures it is a gas which dissolves readily in water. An aqueous solution of formaldehyde, commercially known as "formalin," is largely used as an antiseptic and disinfectant. This solution contains about 40 per cent. of formaldehyde, $HCOH$, and is a liquid of suffocating odour. When evaporated over sulphuric acid, a polymeride, $C_3H_6O_3$, *paraformaldehyde,* is formed; and when allowed to remain in contact with lime-water, another polymeride, $C_6H_{12}O_6$, *formose,* is produced, which is a mixture of sugars. This polymerisation of an aldehyde is of interest as suggesting methods for preparing sugars by synthesis.

Acetic Acid, CH_3COOH (Methyl-formic acid). Obtained by oxidizing ethyl alcohol and in other ways. *See* p. 318.

Aldehyde, or *Acetaldehyde,* C_2H_4O, or CH_3COH.

Experiment.—Place together, in a capacious test-tube (or flask), about four parts of potassium bichromate and twelve of water; cautiously mix four parts of alcohol with five of concentrated sulphuric acid, and allow the mixture to flow slowly through a stopcock funnel on to the contents of the tube, and gently warm the mixture; aldehyde (*al*cohol *dehyd*rogenatum), a highly volatile liquid, is immediately formed, and its vapour evolved, recognisable by its peculiar, somewhat fragrant odour. Adapt a cork and rather long bent tube to the test-tube, and let some of the aldehyde slowly distil over into another test-tube, the condensing-tube being kept as cool as possible. Set the distillate aside for a day or two; the aldehyde will have nearly all disappeared, and acetic acid be found in the tube. Test the remaining liquid by means of litmus-paper; it will be found to have an acid reaction: make it slightly alkaline by adding a drop or two of solution of sodium carbonate, then boil to remove any alcohol and aldehyde present, add sulphuric acid, and notice the characteristic odour of the acetic acid evolved.

These experiments will render the process of oxidation described in connection with acetic acid more easily understood. Pure diluted alcohol is not oxidized by exposure to air alone; but in presence of the ferment, *Mycoderma aceti*, it is oxidized first to aldehyde and then to acetic acid.

In the above process the potassium bichromate and sulphuric acid furnish nascent oxygen, which then acts on the alcohol (just as, in presence of the ferment mentioned above, the oxygen of the air acts on the alcohol in fermented infusion of malt, and in beer or wine), giving aldehyde:—

$$\underset{\text{Alcohol}}{3CH_3CH_2OH} + K_2Cr_2O_7 + 4H_2SO_4$$
$$= \underset{\text{Aldehyde}}{3CH_3COH} + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$$

The aldehyde rapidly, even when pure (more rapidly when impure), absorbs oxygen and yields acetic acid:—

$$\underset{\text{Aldehyde}}{2CH_3COH} + \underset{\text{Oxygen}}{O_2} = \underset{\text{Acetic acid}}{2CH_3COOH}$$

The aldehyde from the above reaction may be mixed with twice its volume of ether, placed in a bottle surrounded by ice, and saturated with dry ammonia; a crystalline compound, *aldehyde-ammonia*, $CH_3{\cdot}CH{\cdot}OH{\cdot}NH_2$, separates. Pure aldehyde may be obtained from this by distilling with dilute sulphuric acid.

Tests.—Aldehyde heated with solution of caustic potash gives a brownish-yellow resinous mass of peculiar odour. Its aqueous solution reduces silver salts giving a mirror-like coating to the inside of a test-tube. When acted on by phenol dissolved in sulphuric acid, it gives a red colour. Aldehyde on keeping, or in contact with sulphuric acid, zinc chloride, etc., yields two polymerides—metaldehyde, xC_2H_4O, and paraldehyde, $C_6H_{12}O_3$, the latter having a characteristic odour. The official paraldehyde (*Paraldehydum*, B.P.) boils at 255·2° F. (124° C.), dissolves in water, alcohol, or ether, is neutral, and should not become coloured on standing for two hours with solution of potassium hydroxide (absence of aldehyde). It may be congealed to a clear crystalline mass which melts at about 50° F. (10° C.).

Chloral

Chloral, or *trichloraldehyde*, CCl_3COH, is a chlorine substitution derivative of aldehyde, though it cannot directly be obtained by acting on aldehyde with chlorine, because condensation products are formed.

Experiment.—Pass a rapid current of dry chlorine into pure absolute alcohol so long as absorption occurs. During the first hour or two the alcohol must be kept cool, and afterwards gradually warmed till ultimately the boiling-point is reached. The crude product is mixed with three times its volume of sulphuric acid and distilled, again mixed with a similar quantity of sulphuric acid and again distilled, and finally rectified from quicklime.

In the formation of chloral it would seem that the substances first formed are hydrochloric acid and aldehyde, the latter of which instantly combines with alcohol to form acetal:—

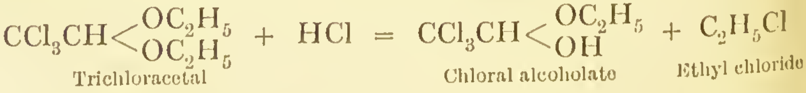
$$\underset{\text{Alcohol}}{CH_3CH_2OH} + \underset{\text{Chlorine}}{Cl_2} = \underset{\text{Aldehyde}}{CH_3COH} + \underset{\text{Hydrochloric acid}}{2HCl}$$

$$\underset{\text{Aldehyde}}{CH_3COH} + \underset{\text{Alcohol}}{2C_2H_5OH} = \underset{\text{Acetal}}{CH_3{\cdot}CH{\cdot}(OC_2H_5)_2} + \underset{\text{Water}}{H_2O}$$

Acetal* by further chlorination yields trichloracetal:—

$$\underset{\text{Acetal}}{CH_3{\cdot}CH(OC_2H_5)_2} + \underset{\text{Chlorine}}{3Cl_2} = \underset{\text{Trichloracetal}}{CCl_3CH{\cdot}(OC_2H_5)_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid}}}{3HCl}$$

Trichloracetal when acted on by the hydrochloric acid yields ethyl chloride and chloral alcoholate:—



$$\underset{\text{Trichloracetal}}{CCl_3CH<\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}} + HCl = \underset{\text{Chloral alcoholate}}{CCl_3CH<\begin{matrix}OC_2H_5\\OH\end{matrix}} + \underset{\text{Ethyl chloride}}{C_2H_5Cl}$$

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* *Methylal*, $CH_2(OCH_3)_2$, the lowest member of the series, is occasionally used as a soporific.

From the alcoholate, *trichlor-aldehyde* or *chloral* is liberated by treatment with sulphuric acid :—

$$\underset{\text{Chloral alcoholate}}{CCl_3{\cdot}CH{\cdot}(OC_2H_5)OH} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Chloral}}{CCl_3COH} + \underset{\text{Ethyl-hydrogen sulphate}}{C_2H_5HSO_4} + \underset{\text{Water}}{H_2O}$$

Properties.—Chloral is a colourless liquid, of oily consistence. Sp. gr. 1·502. Boiling-point 201·2° F. (94° C.). Its vapour has a penetrating smell, and is somewhat irritating to the eyes. When mixed with water, heat is disengaged, and solid, white, crystallizable, *chloral hydrate,* $CCl_3CH(OH)_2$ (*Chloral Hydras,* B.P.), results. "Chloral hydrate" is a true glycol, its systematic name being trichlorethylidene glycol :—

$$\underset{\text{Ethylene glycol}}{C_2H_4(OH)_2} \qquad\qquad \underset{\text{Trichlorethylidene glycol}}{CCl_3CH(OH)_2}$$

Chloral hydrate fuses easily when heated, solidifies at about 120° F. (48·9° C.), boils at from 202° to 206° F. (94·4° to 96·7° C.). It sublimes as a white crystalline powder. Both chloral and chloral hydrate are soluble in water, alcohol, ether, chloroform, and oils. Oils and fats are also soluble in chloral hydrate. The aqueous solution should be neutral, and should give no reaction with silver nitrate. Chloral, especially if it contains a trace of acid, may undergo a spontaneous change into an opaque white isomeric modification, *metachloral,* insoluble in water, alcohol, or ether, but convertible by prolonged contact with water, or by distillation, into the ordinary condition. By action of dilute alkalies chloral yields alkali-metal formate and chloroform :—

$$CCl_3COH + KOH = H{\cdot}CO{\cdot}OK + CHCl_3$$

Chloral, or rather concentrated aqueous solution of chloral hydrate (3 in 4), injected beneath the skin yields chloroform, and produces narcotic effects (Liebreich, Personne). Chloroform itself admits of similar hypodermic use (Richardson). If administered by the stomach, thirty to eighty grains of solid hydrate are required. The final products of the reaction of the chloroform and blood are sodium formate and chloride. A concentrated alcoholic solution of caustic potash effects an analogous change :—$CHCl_3 + 4KOH = H{\cdot}COOK + 3KCl + 2H_2O$.

Solution of ammonia and moist calcium hydroxide, as well as weak solutions of fixed alkalies, convert chloral hydrate into a metallic formate and chloroform. The reaction with the slaked lime being especially definite and complete

(Wood), it may be employed in ascertaining the quantity of chloral hydrate in a sample of the commercial article.

$$\underbrace{2CCl_3CH(OH)_2}_{2 \times 164 \cdot 15} + Ca(OH)_2 = \underbrace{2CHCl_3}_{2 \times 118 \cdot 48} + (HCOO)_2Ca + 2H_2O$$

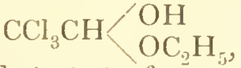
From the foregoing equation and molecular weights, it is obvious that 100 grains of chloral hydrate, if quite dry, will yield by distillation with 30 grains of slaked lime and an ounce of distilled water (in a small flask with a long bent tube kept cool by moistened paper) 72·18 grains of chloroform by weight or (the sp. gr. of chloroform being taken at 1·493), about 52 minims.

Small quantities of chloral hydrate in dilute solutions may be determined by converting its chlorine into a soluble chloride by treatment with zinc and acetic acid, and titrating with volumetric solution of silver nitrate (Short). A quantity of solution containing not more than 0·05 gramme is placed in a small flask with granulated zinc and acetic acid, and allowed to stand twenty-four hours; the solution is then poured off and the zinc washed two or three times with distilled water, a little potassium chromate added, and it is then titrated with deci-normal silver nitrate solution in the usual way, the acetic acid and zinc acetate not interfering with the indications. 1000 c.c. of the silver solution indicate 5·47 of chloral hydrate.

Pure Chloral Hydrate.—Liebreich, who first proposed the use of chloral hydrate, gives the following as the characteristics of the pure article:—Colourless, transparent crystals. Does not decompose by the action of the atmosphere, does not leave oily spots when pressed between blotting-paper, affects neither cork nor paper. Smells agreeably aromatic, but a little pungent when heated. Tastes bitter, astringent, slightly caustic. Seems to melt on rubbing between the fingers. Dissolves in water like candy without first forming oily drops; and the solution is neutral or faintly acid to test-paper. Dissolves in carbon bisulphide, petroleum, ether, water, alcohol, oil of turpentine, etc. Its solution in chloroform gives no colour when shaken with sulphuric acid. Boiling-point 203° to 205° F. (95° to 96·1° C.). It volatilizes without residue. Distilled with sulphuric acid, the chloral should pass over at 205° to 207° F. (96·1° to 97·2° C.). It melts at 133° to 136° F. (56° to 57·7° C.), again solidifying at about 120° F. (48·8° C.). Gives no chlorine reaction on treating the solution in water (acidulated with nitric acid) with silver nitrate.

Impure Chloral Hydrate.—Yellowish, cloudy. Decomposes; leaves spots when pressed between blotting-paper; attacks corks and the paper of the packing. Has a pungent and irritating smell; on opening the bottle is sticky and often emits fumes. Taste strongly caustic. With water forms oily drops or is partially insoluble. Boils at a higher temperature. On treatment with sulphuric acid it turns brown, with liberation of hydrochloric acid. Gives chloride reaction on treating the solution in water (acidulated with nitric acid) with silver nitrate.

Chloralose, $C_8H_{11}Cl_3O_6$, is a derivative of chloral, prepared by heating together anhydrous chloral and glucose, then extracting with ether, and repeatedly distilling with water.

Chloral alcoholates are obtained on combining alcohols with chloral. Chloral alcoholate or trichlorethylidene ethyl ether,  $CCl_3CH\langle{}^{OH}_{OC_2H_5}$, is obtained by mixing alcohol with chloral, it is in fact "chloral hydrate" with one hydroxyl group replaced by (OC_2H_5).

Hirschsohn's test for chloral alcoholate in chloral hydrate is as follows:—Add to 1 gramme of chloral hydrate 1 c.c. of nitric acid of sp. gr. 1·38; in the presence of chloral alcoholate yellow vapours or a yellow liquid will result at ordinary temperatures, or on warming.

Bromal, CBr_3COH, *bromal hydrate*, $CBr_3CH(OH)_2$, and *bromal alcoholates*, are produced when bromine is employed instead of chlorine in the interaction with alcohol. *Iodal*, CI_3COH, is also known.

Butyl Chloral, $C_3H_4Cl_3COH$, originally, but erroneously, termed *croton chloral*, is a product of the action of dry chlorine on cold aldehyde. *Butyl-chloral hydrate* (*Butyl-Chloral Hydras*, B.P.) or *hydrous butyl chloral* (wrongly called *croton-chloral hydrate*), $C_3H_4Cl_3CH(OH)_2$ (*trichlorbutylidene glycol*), occurs "in pearly white trimetric laminæ, having a pungent but not acrid odour, and an acrid nauseous taste. It fuses at about 172° F. (77·8° C.) to a transparent liquid, which, in cooling, commences to solidify at about 160° F. (71·1° C.). Soluble in about 50 parts of water, and in its own weight of glycerin or of alcohol (90 per cent.); it slowly dissolves in 20 parts of chloroform. The aqueous solution is neutral or but slightly acid to litmus. It does not yield chloroform when heated with solution of potassium hydroxide or with milk of lime (absence of chloral hydrate)."

The Acetic Series of Acids—continued.

Propionic Acid (ethyl-formic acid), C_2H_5COOH, is produced by oxidation of propyl alcohol.

Butyric Acid (propyl-formic acid), C_3H_7COOH, is formed by general methods; also during the fermentation of cheese. It is found as a glyceryl salt in butter (whence the name butyric acid).

Valerianic or *Valeric Acid*, C_4H_9COOH.—There are several isomeric varieties of this acid, the valerianic acid from valerian and angelica root, and that artificially formed from amyl alcohol (*see* p. 491) being isovalerianic acid, or isopropyl-acetic acid, $CH(CH_3)_2CH_2 \cdot COOH$, the normal acid having the constitution $CH_3CH_2CH_2CH_2 \cdot COOH$.

Palmitic Acid, $C_{15}H_{31}COOH$, from fats; *stearic acid*, $C_{17}H_{35}COOH$, from suet; *cerotic acid*, $C_{26}H_{53}COOH$, from beeswax; and *melissic acid*, $C_{29}H_{59}COOH$, from beeswax and from carnauba wax (from the surface of the leaves of *Copernicia cerifera*, a Brazilian palm), belong to the acetic series.

The Lactic Series.

Acids of the Lactic Series, $C_nH_{2n}(OH)COOH$.—This series embraces hydroxy-derivatives of the acetic series, one atom of hydrogen being replaced by the hydroxyl group.

$$\underset{\text{Acetic acid}}{CH_3COOH} \qquad \underset{\text{Hydroxyacetic or glycollic acid}}{CH_2(OH)COOH}$$

Though they possess only one carboxyl (COOH) group, yet, having an alcoholic hydroxyl group, they may sometimes have two of their hydrogen atoms replaced by metals.

They are best formed by hydrolysis of the nitriles produced by the union of hydrocyanic acid with aldehydes or ketones; also by partial oxidation of glycols with dilute nitric acid; and by acting on monochloro-derivatives of the acids of the acetic series with moist silver oxide:—

$$\underset{\text{Monochloracetic acid}}{2CH_2Cl \cdot COOH} + Ag_2O + H_2O = \underset{\text{Glycollic acid}}{2CH_2OH \cdot COOH} + 2AgCl$$

TABLE SHOWING THE RELATIONS OF THE CHIEF ACIDS OF THE ACETIC, LACTIC, AND GLYOXYLIC SERIES.

Acids of the Acetic Series, $C_nH_{2n+1}CO\cdot OH$.		Acids of the Hydroxyacetic or Lactic Series, $C_nH_{2n}(OH)CO\cdot OH$.		Acids of the Dihydroxyacetic or Glyoxylic Series, $C_nH_{2n-1}(OH)_2COOH$.	
Formic	$H\cdot CO\cdot OH$	Hydroxyformic or Carbonic	$OH\cdot CO\cdot OH$		
Acetic	$CH_3\cdot CO\cdot OH$	Hydroxyacetic or Glycollic	$CH_2OH\cdot CO\cdot OH$	Dihydroxyacetic or Glyoxylic	$CH(OH)_2COOH$
Propionic	$C_2H_5\cdot CO\cdot OH$	Hydroxypropionic or Lactic	$C_2H_4OH\cdot CO\cdot OH$	Dihydroxypropionic or Glyceric	$C_2H_3(OH)_2COOH$
Butyric	$C_3H_7\cdot CO\cdot OH$	Hydroxybutyric	$C_3H_6OH\cdot CO\cdot OH$	Dihydroxybutyric	$C_3H_5(OH)_2COOH$
Valerianic	$C_4H_9\cdot CO\cdot OH$	Hydroxyvalerianic	$C_4H_8OH\cdot CO\cdot OH$		
Caproic	$C_5H_{11}\cdot CO\cdot OH$	Hydroxycaproic or Leucic	$C_5H_{10}OH\cdot CO\cdot OH$		
Œnanthylic	$C_6H_{13}\cdot CO\cdot OH$	Hydroxyœnanthylic	$C_6H_{12}OH\cdot CO\cdot OH$		
Caprylic	$C_7H_{15}\cdot CO\cdot OH$	Hydroxycaprylic	$C_7H_{14}OH\cdot CO\cdot OH$		
Pelargonic	$C_8H_{17}\cdot CO\cdot OH$				
Capric	$C_9H_{19}\cdot CO\cdot OH$				
Lauric	$C_{11}H_{23}\cdot CO\cdot OH$	Hydroxylauric	$C_{11}H_{22}OH\cdot CO\cdot OH$		
Myristic	$C_{13}H_{27}\cdot CO\cdot OH$				
Palmitic	$C_{15}H_{31}\cdot CO\cdot OH$				
Stearic	$C_{17}H_{35}\cdot CO\cdot OH$				
Arachidic	$C_{19}H_{39}\cdot CO\cdot OH$				
Behenic	$C_{21}H_{43}\cdot CO\cdot OH$				
Cerotic	$C_{26}H_{53}\cdot CO\cdot OH$				
Melissic	$C_{29}H_{59}\cdot CO\cdot OH$				

Carbonic Acid or *Hydroxyformic Acid*, $OH{\cdot}CO{\cdot}OH$, the first of this series, has been studied already. *Carbamide* or *Urea*, $NH_2{\cdot}CO{\cdot}NH_2$, the diamide of carbonic acid, is interesting historically as being the first organic compound synthetically produced from inorganic sources (*see* p. 425). The acid amide of carbonic acid, *carbamic acid*, $NH_2{\cdot}CO{\cdot}OH$, occurs as an ammonium salt, $NH_2{\cdot}CO{\cdot}ONH_4$, in the ammonium carbonate of pharmacy. Ethyl carbamate, or *Urethane*, $NH_2{\cdot}CO{\cdot}OC_2H_5$, is a mild hypnotic.

Glycollic Acid (Hydroxyacetic acid), $CH_2OH{\cdot}COOH$, is found in the leaves of the Virginia Creeper; artificially it may be obtained by carefully oxidizing glycol, and by the action of silver oxide on dextrose and fructose.

Lactic Acid (Hydroxypropionic acid), $C_2H_4(OH)COOH$. Several isomeric hydroxypropionic acids are known; the lactic acid of fermentation (so-called ethylidene* lactic acid), $CH_3CH{\cdot}(OH)COOH$, and sarcolactic acid, from flesh, being those of technical importance (*see* p. 379).

The Acrylic Series.

Acids of the Acrylic Series, $C_nH_{2n-1}COOH$.

Acrylic Acid, C_2H_3COOH, or $CH_2 : CH{\cdot}COOH$, is formed by oxidizing acrolein (acrylaldehyde, *see* Glycerin) with silver oxide.

Crotonic Acid, C_3H_5COOH, or $CH_3CH : CH{\cdot}COOH$, formerly supposed to be a constituent of croton oil, may be formed by oxidizing croton-aldehyde, and by acting on allyl cyanide, C_3H_5CN, with water and hydrochloric acid:—

$C_3H_5CN + 2H_2O + HCl = C_3H_5CO{\cdot}OH + NH_4Cl$.

Oleic Acid, $C_{18}H_{34}O_2$, is found as a glyceryl salt in many fats and oils.

Preparation of Oleic Acid.—Olive oil is saponified by means of caustic potash and the resulting soap decomposed by tartaric acid, which liberates oleic and stearic acids. The oleic and stearic acids are heated with lead oxide, forming lead oleate and stearate, the former being dissolved out from the latter by ether. The ether is evaporated and the lead oleate treated with hydrochloric acid, which liberates oleic acid.

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* Substances having the CH_3CH group are called ethylidene compounds. Compare chloral hydrate, trichlor*ethylidene* glycol, $CCl_3CH{\cdot}(OH)_2$.

Elaidic Acid (isomeric with oleic acid) is formed by passing nitrogen peroxide into oleic acid; it is more stable than oleic acid, distilling unchanged.

The Benzoic Series.

Acids of the Benzoic Series, $C_nH_{2n-7}COOH$.—The acids of this series are formed by oxidizing hydrocarbons, by the oxidation of the corresponding alcohols, and by the hydrolysis of the corresponding nitriles. There are numerous isomers of all these acids, benzoic acid excepted.

Benzoic Acid, C_6H_5COOH, occurs naturally in gum benzoin (Gum Benjamin), which contains from 12 to 15 per cent., the remainder of the "gum" being mainly composed of two resins having the formulæ $C_{40}H_{46}O_9$ and $C_{30}H_{40}O_5$. Benzoic acid may be obtained by oxidizing benzaldehyde, C_6H_5COH, which may be prepared from benzotrichloride (*see* p. 472). Toluene, $C_6H_5CH_3$, may be directly oxidized into benzoic acid, the methyl group (CH_3) being resolved into COOH. Benzoic acid may also be produced by heating hippuric acid (benzoyl glycine or benzoyl glycocoll) with hydrochloric acid, p. 372. For other modes of obtaining benzoic acid artificially, *see* p. 367. Benzoic acid heated with lime yields benzene:—

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + \underset{\text{Calcium oxide}}{CaO} = \underset{\text{Benzene}}{C_6H_6} + \underset{\text{Calcium carbonate}}{CaCO_3}$$

Benzaldehyde, C_6H_5COH, forms the greater part of oil of bitter almonds (*see* Amygdalin, p. 576). It is a colourless liquid, soluble in 30 parts of water, and in all proportions in ether and alcohol. Like other aldehydes, it forms a crystalline compound with acid sodium sulphite—in this case $C_6H_5{\cdot}COH{\cdot}NaHSO_3$.

Benzoyl Chloride, C_7H_5OCl, results from the action of chlorine on benzaldehyde or of phosphorus pentachloride on benzoic acid. Benzaldehyde also results from the oxidation of the benzyl alcohol (C_7H_7OH) of balsam of Peru.

The Hydroxybenzoic Series.

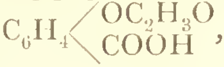
Acids of the Hydroxybenzoic Series, $C_nH_{2n-8}OH{\cdot}COOH$.—Just as the acids of the lactic series are related to the acetic series, so are the acids of the hydroxybenzoic (or salicylic) series related to the benzoic series.

CH_3COOH Acetic acid	$CH_2OH{\cdot}COOH$ Hydroxyacetic or glycollic acid
C_6H_5COOH Benzoic acid	$C_6H_4OH{\cdot}COOH$ Ortho-hydroxybenzoic or salicylic acid

Salicylic or *Ortho-hydroxybenzoic Acid*, $C_6H_4OH{\cdot}COOH$ (*Acidum Salicylicum*, B.P.). Salicylic acid may be made by the oxidation of salicylaldehyde (*vide infra*). Sodium salicylate may be prepared by the action of carbonic anhydride on sodium-phenol (Kolbe). To accomplish this, phenol is mixed with caustic soda, forming sodium-phenol, or sodium carbolate, C_6H_5ONa. The sodium phenol is then saturated with carbonic anhydride at the ordinary temperature, by which sodium phenyl carbonate is produced. The latter on being heated in closed vessels is transformed into sodium salicylate. From this salicylic acid may be obtained by the action of hydrochloric acid, and it may be purified by recrystallization from alcohol. It is identical with the natural acid.

$$\underset{\text{Sodium-phenol}}{C_6H_5{\cdot}ONa} + CO_2 = \underset{\text{Sodium phenylcarbonate}}{C_6H_5O{\cdot}CO{\cdot}ONa}$$

$$\underset{\substack{\text{Sodium}\\\text{phenylcarbonate}}}{C_6H_5O{\cdot}CO{\cdot}ONa} = \underset{\substack{\text{Sodium}\\\text{salicylate}}}{C_6H_4OH{\cdot}CO{\cdot}ONa}$$

Salicylic acid, like carbolic acid, is a powerful antiseptic but is free from the taste and smell of carbolic acid. It is only slightly soluble in cold water, but readily soluble in hot water, alcohol, ether, and in aqueous solutions of such alkali-metal salts as borax, sodium phosphate, or potassium citrate, which it converts into acid salts with formation of a salicylate. A similar antiseptic *cresotic acid* (hydroxytoluic acid, $C_6H_3OH{\cdot}CH_3{\cdot}COOH$) is similarly obtained from cresol or cresylic acid, $C_6H_4OH{\cdot}CH_3$. Ferric chloride produces a violet coloration with both salicylic and cresotic acids. Both acids have antipyretic properties. The alkali-metal salicylates, and probably therefore the cresotates, are very feeble antiseptics. Sodium salicylate (*Sodii Salicylas*, B.P.), $(NaC_7H_5O_3)_2,H_2O$, made by neutralizing salicylic acid with sodium hydroxide or carbonate, forms small, colourless scales, or tabular crystals, soluble in alcohol, and readily soluble in water. As carbolic acid often contains cresylic acid, commercial salicylic acid may contain cresotic acid. An alcoholic solution of salicylic acid allowed to evaporate spontaneously (exposure to dust being avoided), should leave a white residue free from colour even at the points of the crystals. *Iodosalicylic acid*, $C_7H_5IO_3$, and *di-iodosalicylic acid*, $C_7H_4I_2O_3$, are used in medicine; as also is acetylsalicylic acid,  $C_6H_4\left\langle\substack{OC_2H_3O\\COOH}\right.$, which is known as *aspirin.*

Salicylaldehyde, or ortho-hydroxybenzaldehyde (salicylol, salicylous acid, salicyl hydride), $C_6H_4OH{\cdot}COH$.—Found in the essential oil of meadow-sweet (*Spiræa ulmaria*); also obtained by the oxidation of salicin. It may be artificially formed by the action of chloroform on sodium phenol.

Preparation.—Mix 10 parts of phenol with 20 parts of sodium hydroxide dissolved in 30 parts of water in a flask having an upright condenser, and gradually add 20 parts of chloroform. After heating the flask on a water-bath, until all chloroform has disappeared, add excess of hydrochloric acid, when a red-violet oil will rise to the surface. Pour the contents of the flask into a retort, and pass steam through it till no more aldehyde comes over. The reaction is as follows:—

$$\underset{\text{Sodium phenol}}{C_6H_5ONa} + 3NaOH + \underset{\text{Chloroform}}{CHCl_3} = \underset{\text{Sodium salicyl-aldehyde}}{C_6H_4ONa{\cdot}COH} + 3NaCl + 2H_2O$$

Sodium salicylaldehyde, treated with hydrochloric acid and distilled, gives salicylaldehyde:—

$$\underset{\text{Sodium salicyl-aldehyde}}{C_6H_4ONa{\cdot}COH} + HCl = \underset{\text{Salicylaldehyde}}{C_6H_4(OH)COH} + NaCl$$

The oil which passes over (orthohydroxybenzaldehyde) may be purified from phenol (with which it is always contaminated) by treating with acid sodium sulphite, which forms a compound with the aldehyde, leaving the phenol which may be removed by dissolving it in ether. An isomeric salicylaldehyde (parahydroxybenzaldehyde) is formed along with the ortho-aldehyde, and remains dissolved in the water in the retort, from which it is precipitated on cooling.

Methyl Salicylate, $CH_3C_7H_5O_3$, formerly known as "gaultheric acid," forms the chief part, at least 90 per cent., of the essential oil of gaultheria (*Oleum Gaultheriæ*, B.P., Add. 1900) or winter-green (*Gaultheria procumbens*, the fresh leaves of which yield about 0·4 per cent. of oil). It also occurs in several species of violet (Mandelin). Oil of sweet birch

(*Betula lenta*) is methyl salicylate. Gaultherin, a glucoside existing in the bark of Betula lenta, when decomposed by mineral acids, by alkalies, or by heating the aqueous solution to 130°-140° C., yields a carbohydrate and methyl salicylate. *Methyl Salicylas,* U.S.P., is produced synthetically.

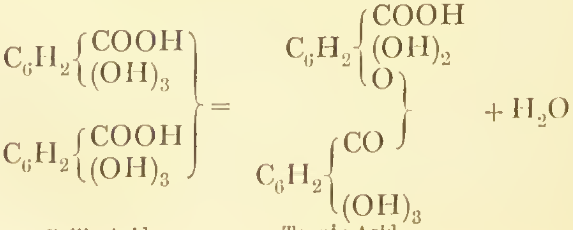
Phenyl Salicylate, $C_6H_4OH{\cdot}CO{\cdot}OC_6H_5$, or *salol* (*Salol,* B.P.), is an antiseptic, antipyretic, anti-rheumatic remedy. It is white, crystalline, soluble in alcohol, almost insoluble in water, and has a faint aromatic odour.

Orthoform, a new anaesthetic, is the methyl ester of para-amido-meta-hydroxybenzoic acid.

VANILLIN OR METHYLPROTOCATECHUIC ALDEHYDE, $C_8H_8O_3$ or $C_6H_3(OH)(OCH_3)CHO$, is the substance to which the odour and flavour of vanilla are due. It also occurs in Siam benzoin, *Rosa canina,* etc. The white crystals commonly found on vanilla (the prepared unripe pods of *Vanilla planifolia*), termed *vanillin,* were found by Carles to be a weak acid. It occurs in vanilla to the extent of from 1½ to 3 per cent. Vanillin has in recent years been prepared artificially by Tiemann and Haarmann from coniferin, a glucoside existing in the sapwood of pines. The substance remaining after the removal of glucose from coniferin, or, indeed, coniferin itself, by action of a mixture of potassium bichromate and sulphuric acid, yields vanillin. It may also be obtained by a series of reactions starting from that of carbonic anhydride on potassium carbolate; also from the eugenol of oil of cloves. By action of hydrochloric acid, vanillin yields methyl chloride and protocatechuic aldehyde. Artificial vanillin is now manufactured by various patented methods.

The Trihydroxybenzoic Series.

Acid of the Series, $C_nH_{2n-10}(OH)_3COOH$. *Gallic Acid,* or trihydroxybenzoic acid, $C_6H_2(OH)_3COOH$ (*see* p. 393). By the elimination of one molecule of water from two molecules of gallic acid, tannic acid is produced.



$$\left.\begin{array}{l} C_6H_2\begin{cases}COOH\\(OH)_3\end{cases}\\ C_6H_2\begin{cases}COOH\\(OH)_3\end{cases}\end{array}\right\} = \begin{array}{l} C_6H_2\begin{cases}COOH\\(OH)_2\\O\end{cases}\\ C_6H_2\begin{cases}CO\\(OH)_3\end{cases}\end{array} + H_2O$$

Gallic Acid Tannic Acid

Gallic acid, by the action of heat yields *pyrogallol* or *pyrogallic acid* and carbonic anhydride.

$$C_6H_2(OH)_3COOH = C_6H_3(OH)_3 + CO_2$$

The Cinnamic Series.

Acids of the Cinnamic Series, $C_nH_{2n-9}COOH$.—Cinnamic acid, C_8H_7COOH, may be obtained from the balsams of tolu and Peru, and from storax. It may be made artificially by aid of Perkin's reaction, which consists in heating 2 parts of benzaldehyde with 3 of acetic anhydride and one of sodium acetate.

1. *Balsam of Peru* (*Balsamum Peruvianum,* B.P.), an exudation from the trunk of *Myroxylon Pereiræ,* is a mixture of oily matter with about one-quarter or one-third of resinous matter and 6 per cent. of cinnamic acid. The oil, by fractional distillation in an atmosphere of carbonic anhydride, under diminished pressure, furnishes *benzyl alcohol,* $C_6H_5CH_2OH$, *benzyl benzoate,* $C_6H_5CO{\cdot}OC_7H_7$, and *benzyl cinnamate,* $C_8H_7CO{\cdot}OC_7H_7$, or *cinnamein* (Kraut). By action of alcoholic solution of caustic potash it yields potassium benzoate and cinnamate, and benzyl alcohol; also *cinnamyl alcohol,* $C_8H_7CH_2OH$, otherwise known as *peruvine* or *styrone.* It also often holds in solution *metacinnamein* or *styracin,* $C_{18}H_{16}O_2$, polymeric with cinnamaldehyde, C_8H_7COH. The resin of balsam of Peru seems to result from the action of moisture on the oil. Any admixture of resin, oil, storax, benzoin, or copaiba, with balsam of Peru is detected by mixing 6 grains of slaked lime with 10 drops of the balsam, when a soft product results if the specimen be pure, but hard, if impure; further, the mixture, on being warmed until volatile matter is expelled and charring commences, gives no fatty odour. 2. *Balsam of Tolu* (*Balsamum Tolutanum* B.P.) is an exudation from the trunk of *Myroxylon Toluifera;* in composition it closely resembles balsam of Peru, but is more easily resinified. It contains benzyl benzoate and cinnamate, cinnamic acid, a small proportion of benzoic acid (Busse), and about 1 per cent. of a volatile hydrocarbon, *tolene,* $C_{10}H_{16}$. The cinnamic acid crystals may be seen with a lens when a little of the balsam is pressed between two warmed pieces of glass. Old hard balsam of tolu is a convenient source of cinnamic acid, which may be extracted by the same process as that by which benzoic acid is obtained from benzoin—namely, ebulli-

tion with alkali, filtration, and precipitation by addition of hydrochloric acid. In syrup of tolu the cinnamic acid is liable, if certain micro-organisms are present, to develop carbonic anhydride and acetylene, the latter communicating an unpleasant smell, $C_9H_8O_2 = CO_2 + 4C_2H_2$. 3. *Storax* is an oleo-resin obtained from *Liquidambar orientalis.* It contains a volatile oil termed *styrol, cinnamene,* or *cinnamol,* C_8H_8,—which possibly (Berthelot) is condensed acetylene, $4C_2H_2$,—cinnamic acid, styracin, or cinnamyl cinnamate, $C_8H_7CO{\cdot}OC_9H_9$, and a soft and a hard resin. Styrol differs from similar hydrocarbons in being converted into a polymeric solid, termed *metastyrol* or *draconyl,* on heating to about 400° F. (204·4° C.). For medicinal use, storax (*Styrax Præparatus,* B.P.) is purified by solution in alcohol, filtration, and removal of the alcohol by distillation. By oxidation with potassium bichromate and sulphuric acid it yields an odour resembling that of essential oil of bitter almonds.

Coumarin, $C_9H_6O_2$ (the principle of the Tonka bean), may be obtained by acting on the sodium-derivative of salicylaldehyde with acetic anhydride and sodium acetate (Perkin).

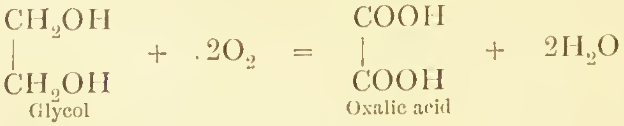
Dibasic Acids.

These have two carboxyl (COOH) groups in the molecule.

The Succinic Series.

Acids of the Succinic Series, $C_nH_{2n}(COOH)_2$.—These acids may be formed by the oxidation of glycols, or by the action of water and hydrochloric acid on the cyanides of the olefines, obtained by acting on the olefine dibrom-addition products with potassium cyanide.

Oxalic Acid, $H_2C_2O_4$ or $(COOH)_2$, is the first of this series. It may be obtained by oxidizing glycol, $C_2H_4(OH)_2$—



$$\underset{\text{Glycol}}{\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}} + 2O_2 = \underset{\text{Oxalic acid}}{\begin{matrix}COOH\\|\\COOH\end{matrix}} + 2H_2O$$

Also by the action of carbonic anhydride on sodium :—

$$\underset{\text{Carbonic anhydride}}{2CO_2} + \underset{\text{Sodium}}{2Na} = \underset{\text{Sodium oxalate}}{Na_2C_2O_4}$$

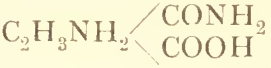
For other methods, *see* Oxalic Acid, p. 344.

Oxamide, $C_2O_2(NH_2)_2$, the analogue of urea,—carbamide, $CO(NH_2)_2$,—is formed on mixing ethyl oxalate with solution of ammonia; or by passing cyanogen into aqueous hydrochloric acid, $C_2N_2 + 2H_2O = (CONH_2)_2$.

Succinic Acid, $C_2H_4(COOH)_2$. (*See* p. 389.)

The Malic Series.

Acids of the Malic Series, $C_nH_{2n-1}OH(COOH)_2$.—Malic, or hydroxysuccinic acid, $C_2H_3(OH)\ (COOH)_2$, is obtained artificially by acting on bromosuccinic acid, $C_2H_3Br(COOH)_2$, with moist silver oxide, the bromine being replaced by hydroxyl. It is contained in unripe mountain-ash berries, morello cherries, etc. (*See* p. 379.)

Asparagin (amidosuccinamic acid), 
$C_2H_3NH_2\left\langle\begin{matrix}CONH_2\\COOH\end{matrix}\right.$
(*See* p. 380.)

The Tartaric Series.

Acids of the Tartaric Series, $C_nH_{2n-2}(OH)_2(COOH)_2$.—*Tartaric Acid*, (dihydroxysuccinic acid), $C_2H_2(OH)_2(COOH)_2$, may be obtained by oxidizing erythrite, $C_2H_2(OH)_2(CH_2OH)_2$. (*See* p. 516.) For other modes of formation, *see* p. 347. There are four isomeric tartaric acids, differing in their relation to polarized light.

The Phthalic Series.

Acids of the Phthalic Series, $C_nH_{2n-8}(COOH)_2$.—*Phthalic Acid*, $C_6H_4(COOH)_2$, is obtained by the oxidation of napthalene and naphthalene tetrachloride, or a mixture of benzene and benzoic acid. By distillation it forms phthalic anhydride, $C_8H_4O_3$, and this when heated with phenol and sulphuric acid yields *phenol-phthalein* (B.P.), a light yellow crystalline powder, which when dissolved in alcohol is used in alkalimetry on account of its property of turning reddish-purple in presence of the slightest excess of alkali. There are three phthalic acids, ordinary phthalic or orthophthalic acid, isophthalic or metaphthalic acid, and terephthalic or paraphthalic acid. (*See* p. 474.)

TRIBASIC ACIDS.

These have three carboxyl (COOH) groups in the molecule. *Tricarballylic Acid*, or propane-tricarboxylic acid, $C_3H_5(COOH)_3$, is the first of these acids; its hydroxy-derivative is *citric acid*, $C_3H_4(OH)(COOH)_3$ (hydroxy-propane-tricarboxylic acid), found in a variety of fruits. It has already been described (*see* p. 351).

TABLE SHOWING THE RELATIONS BETWEEN ACIDS OF THE ACETIC SERIES AND THE DIBASIC ACIDS.

Acids of the Acetic Series, $C_nH_{2n+1}COOH$	Acids of the Succinic Series, $C_nH_{2n}(COOH)_2$	Acids of the Hydroxysuccinic or Malic Series, $C_nH_{2n-1}(OH)(COOH)_2$	Acids of the Dihydroxysuccinic or Tartaric Series, $C_nH_{2n-2}(OH)_2(COOH)_2$
Formic, $H·CO·OH$	Oxalic, $COOH·COOH$	—	—
Acetic, $CH_3·CO·OH$	Malonic, $CH_2(CO·OH)_2$	Tartronic (oxymalonic), $CH·OH·(COOH)_2$	Mesoxalic, $C(OH)_2(COOH)_2$
Propionic, $C_2H_5·CO·OH$	Succinic, $C_2H_4(CO·OH)_2$	Malic (Oxysuccinic), $C_2H_3·OH·(COOH)_2$	Tartaric (or dioxysuccinic), $C_2H_2(OH)_2(COOH)_2$
Butyric, $C_3H_7·CO·OH$	Glutaric, $C_3H_6(CO·OH)_2$	Oxyglutaric, $C_3H_5·OH·(COOH)_2$	Homotartaric, $C_3H_4(OH)_2(COOH)_2$

OTHER POLYBASIC ACIDS

Tetrabasic acids—as pyromellitic acid, $C_6H_2(COOH)_4$—and *hexabasic* acids—as mellitic acid, $C_6(COOH)_6$—are known.

KETONES

Just as primary alcohols on losing hydrogen by oxidation yield aldehydes, so secondary alcohols (*see* p. 482) yield ketones :—

$$C_nH_{2n+1}CH_2OH \ - \ H_2 \ = \ C_nH_{2n+1}COH \text{ (aldehyde)}$$
$$(C_nH_{2n+1})_2CHOH \ - \ H_2 \ = \ (C_nH_{2n+1})_2CO \text{ (ketone)}$$

Like aldehydes, ketones are converted by reduction with hydrogen into the corresponding alcohols. Like aldehydes, ketones form crystalline compounds with acid sulphites. While, however, aldehydes by oxidation yield corresponding acids, ketones yield acids whose molecules have a smaller number of carbon atoms than the original ketones.

Acetone, C_3H_6O, or *dimethyl-ketone*, $(CH_3)_2CO$ or $CH_3 \cdot CO \cdot CH_3$, the best known of the class, may be obtained by strongly heating calcium acetate, carbonate remaining; $(CH_3COO)_2Ca = (CH_3)_2CO + CaCO_3$. The calcium salts of other fatty acids split up in a similar manner (hence perhaps the name—from *κέω*, *keō*, I split, and the original *acetone*), yielding other ketones, as propione, butyrone, valerone, etc. The mixed calcium salts give corresponding ketones. Thus acetate and caprate yield methy-nonyl ketone, $CH_3—CO—C_9H_{19}$, the chief natural constituent of oil of rue. *Acetophenone* or *phenyl-methyl ketone*, $C_6H_5 \cdot CO \cdot CH_3$, is known as *hypnone*.

QUESTIONS AND EXERCISES

Give general methods for the formation of aldehydes and acids.—How is acetaldehyde prepared?—Describe the reactions that occur in the manufacture of chloral and chloral hydrate.—What is the nature of the action of alkalies on chloral hydrate?—Mention the characters of pure and impure chloral hydrate.—What relation has valerianic acid to amyl alcohol?—Give the relations between the acetic and lactic series of acids.—To what series do the following acids belong:—oleic, butyric, oxalic, and citric?—How is benzoic acid prepared? Give the differences between balsam of Peru, tolu, and gum benzoin.—How is oil of bitter almonds prepared, and how can it be distinguished from so-called artificial oil of bitter almonds?—Give methods of preparing artificial salicylic aldehyde and acid.—Give systematic names for tartaric, succinic, carbonic, salicylic, and citric acids.

Volatile Oils

The *Volatile* or *Essential Oils* exist in various parts of plants. They usually are mixtures of the liquid hydrocarbons or *elæoptens* (from ἔλαιον, *elaion*, oil, and ὄπτομαι, *optomai*, to see) with oxidized hydrocarbons, which are commonly solid or camphor-like bodies termed *stearoptens* (from στέαρ, *stear*, suet), and which on cooling often crystallize out; or on distilling an oil the stearopten may remain in the retort being less volatile than the elæopten. The volatile oils often are associated with further oxidized substances termed *resins*.

The tendency of the results of recent investigations is to show that instead of the characteristic odour of an essential oil being due to one single principal constituent, the other bodies present have a distinct influence in determining the odour. Oils of caraway, anise and linaloe are examples of those in which the aroma is due to a single odorous substance,—carvone, anethol, and linalool; but in many volatile oils the conditions are more complex. Rose oil affords a striking example of the important influence which combinations of odoriferous bodies sometimes exercise on the perfume; the oils of rose, geranium, and palmarosa contain approximately the same percentage of geraniol, which is identical in the three oils. Whilst, however, geranium and palmarosa oils are valued in proportion to the amount of geraniol they contain, the value of rose oil depends upon the various other substances present.

The process by which volatile oils are usually obtained from herbs, flowers, fruits, or seeds, may be imitated on the small scale by placing the material (bruised cloves or caraways, for instance) in a tubulated retort, adapting the retort to a Liebig's condenser, and passing steam, from a flask, through a glass tube to the bottom of the warmed retort. The steam in its passage through the substance takes up some of the vapour of the oil and carries it into the condenser, whence, cooled and liquefied, it flows, along with the condensed water, into the receiving vessel, where it will be found floating on the water. It may be collected by running off the distillate through a glass funnel having a stopcock in the stem, or by letting the water from the condenser drop into a test-tube or similar tube which has a small hole in the bottom, and is placed in a larger vessel containing water, the water and oil being subsequently run off separately from the tube as from a pipette. The water will in most cases be the ordinary official medicated water of the material operated on (*Aqua Anethi, Anisi, Aurantii Floris, Carui, Cinnamomi, Fœniculi, Menthæ Piperitæ, Menthæ Viridis, Pimentæ, Rosæ, Sambuci*). Volatile oils, like fixed oils, stain paper; but the stain of the former is not permanent like that of the latter. Oils of lemon and orange are sometimes obtained by mere pressure of the rind of the fruit. Volatile oils are "concentrated" by removing inodorous terpene, whereby the so-called terpeneless oils are obtained.

The presence of alcohol in an essential oil may be detected and its quantity estimated by shaking with an equal bulk of pure glycerin. The latter dissolves the alcohol, and is augmented in volume according to the amount of alcohol present (Boettger). (For tests for alcohol, *see* p. 490.)

A large number of volatile oils are employed in medicine, either in the pure state, in the form of saturated aqueous solutions (medicated waters), or solutions in alcohol (*Spiritus Anisi, Cajuputi, Cinnamomi, Juniperi, Lavandulæ, Menthæ Piperitæ, Myristicæ, Rosmarini*), or as leading constituents in various barks, roots, leaves, etc. *Perfumes* ("scents" or "essences," including "lavender-water" and "eau de Cologne") are for the most part solutions of essential oils in alcohol (45 to 90 per cent.), or spirituous infusions of materials containing essential oils. The following oils are, directly or indirectly, included in the Pharmacopœias*:— 1. Volatile oil of *Bitter Almond* (*see* p. 577). 2. Oil of the fruits of *Ajwain* or *Omum, Carum Ajowan*, or *Ptychatis Ajowan* (*Fructus Ptychotis*, P.I.; *Oleum Ajowan*, Ajowan Oil, *Syn.* Ptychotis Oil, distilled from the fruits of *Carum copticum*, B.P. Add. 1900), contains *cymol* or *cymene* ($C_{10}H_{11}$), and a stearopten (*Ajwainka-phul*, flowers of ajwain) identical with *thymol*, $C_{10}H_{14}O$. 3. Oil of *Dill* (*Oleum Anethi*, B.P.), a pale, yellow, pungent liquid of sweetish warm flavour, distilled from dill-fruit; it contains a hydrocarbon, *anethene* ($C_{10}H_{16}$), and an oxidized oil ($C_{10}H_{14}O$) identical with the carvone of oil of caraway (Gladstone). 4. Oil of *Anise* (*Oleum Anisi*, B.P.), a colourless or pale yellow liquid, of sweetish warm flavour, distilled in Europe from the anise fruit (*Pimpinella anisum*), but chiefly in China, from the fruit of star-anise (*Illicium verum*); it is a mixture of a hydrocarbon, isomeric with oil of turpentine, and *anethol*, a stearopten ($C_{10}H_{12}O$) which crystallizes out at low temperatures. The melting point of anethol is 70° F. (21·1° C.) (Moreau and Chauvet). The official Oil of Anise congeals, when stirred, at temperatures between 50° and 59° F. (10° to 15° C.), and should not again become liquid below 59° F. (15° C.). The congealing point of the natural oils appears to be dependent on the proportion of the fluid to the solid constituent, a very small quantity of the former lowering the congealing and melting points very considerably. 5. Oil of *Chamomile* (*Oleum Anthemidis*, B.P.), a bluish or, when old, yellow oil, of characteristic odour and taste, distilled from chamomile-flowers (*Anthemidis Flores*, B.P.). The official variety (*Anthemis nobilis*) yields about 0·2 per cent. of an oil composed of a hydrocarbon ($C_{10}H_{16}$) and an oxidized portion ($C_{10}H_{16}O_2$) which, heated with potash, gives *potassium angelate* ($KC_5H_7O_2$), whence is obtained *angelic acid* ($HC_5H_7O_2$). According to Demarçay, Kopp, and Köbig, the oil is a mixture of butyl and amyl angelates and similar bodies. Naudin has also obtained from chamomiles *anthemen*, a hydrocarbon crystallizing in needles. The flowers of another variety (*Matricaria chamomilla*) contain a stearopten ($C_{10}H_{16}O$) having the composition of laurel-camphor. 6. Oil of *Horse-radish* root (*Armoraciæ Radix*, B.P.) seems to consist mainly of allyl iso-thiocyanate, C_3H_5NCS: it is the chief active ingredient of *Spiritus Armoraciæ Compositus*, B.P. 7. Oil of *Bitter-Orange* rind (*Aurantii Cortex Recens*, B.P., *Aurantii Cortex Siccatus*, B.P., *Aurantii Cortex Indicus*, B.P., Add. 1900), the flavouring constituent of the official Syrup of Orange (*Syrupus Aurantii*, B.P.), and the oils of various species of *Citrus;* namely:—8. *Lemon* (*Oleum Limonis*, B.P., from *Limonis Cortex*, B.P., the fresh outer part of the pericarp of the fruit of *C. medica*, var. *β Limonum*); 9. *Lime* (Italian, from *C. limetta;* West Indian, from *C. medica*, var. *acida*); 10. *Bergamot* (from *C. bergamia*); 11. *Citron* and a variety of citron termed *cedra*; resemble each other in composition, all containing a variety of limonene (*hesperidene*), a hydrocarbon, $C_{15}H_{24}$, and a small quantity of oxidized hydrocarbons [$C_{10}H_{10}O_5$, $C_{15}H_{16}O$, and (Wright and Piesse) $C_{20}H_{30}O_3$], etc. Lemon oil consists chiefly of a limonene, $C_{10}H_{16}$, boiling at 176° C., together with a small quantity of phellandrene. Its chief aromatic constituents are the aldehydes, citral, $C_{10}H_{16}O$, and citronellal, $C_{10}H_{18}O$. A terpeneless oil of lemon has been described by Geissler, who states that it excels the commercial oil in odour, flavour, and stability. Oil of bergamot appears to owe its fragrance to 40 or 50 per cent. of *linalyl acetate*, $C_{10}H_{17}C_2H_3O_2$. It also contains a stearopten, *bergapten*, $C_{12}H_8O_4$. Expressed lime essence contains a soft resin. 12. Oil of *Neroli*, or *Orange-Flower* (distilled from the flowers of the bitter orange tree, *Citrus Aurantium*, var. *Bigaradia*), the aqueous solution of which is official in the forms of water (*Aqua Aurantii Floris*, B.P.) and syrup (*Syrupus Aurantii Floris*, B.P.), contains a fragrant hydrocarbon ($C_{10}H_{16}$), colourless when fresh, but becoming red on exposure to light, and an inodorous, oxidized hydrocarbon. Strong acids, especially nitric, attack the oil in orange-flower water, imparting to the fluid a rose tint. 13. Oil of *Petit Grain*, distilled from the leaves and shoots of the orange-tree, consists chiefly of *linalyl acetate*, $C_{10}H_{17}C_2H_3O_2$. 14. The leaves of *Boldo* (*Peumus Boldus*), a Chilian shrub (tonic and hepatic), yield 2 per cent. of essential oil (and, according to Bourgon and Verne, an alkaloid, *boldine*). 15. Oil of *Buchu-leaves* (*Buchu Folia*, B.P.) consists chiefly of a fluid oil, $C_{10}H_{18}O$, holding in solution a crystalline stearopten, diosphenol, $C_{10}H_{16}O_2$. 16. Oil of *Cannabis indica*, *see* p. 550. 17. Oil of (the lesser) *Cardamoms*, from the seeds of *Elettaria Cardamomum* (*Cardamomi Semina*, B.P.), freed from their pericarps, is chiefly a hydrocarbon ($C_{10}H_{16}$) isomeric with oil of turpentine (terpilene and probably limonene) and a camphor resembling turpentine-camphor ($C_{10}H_{16},3H_2O$). 18. Oil of *Cajuput* (*Oleum Cajuputi*, B.P.), from the leaves of *Melaleuca Leucadendron*, is a mobile bluish liquid, consisting of *hydrous cajuputene*, *cajuputol*, or *cineol* (*eucalyptol*), $C_{10}H_{17}OH$, and terpineol as well as butyric, valeric, and benzoic aldehydes. Fresh cajuput-oil has a green hue, which is perhaps transient, for the colour of the commercial oil is due to copper (Guibourt and Histed): certainly the green colouring-matter of pure cajuput-oil is organic and either oily or chlorophylloid. 19. Oil of *Caraway*-fruit (*Oleum Carui*, B.P., from *Carui Fructus*, B.P.) is a mixture of *carvone* (formerly called *carvol*) ($C_{10}H_{14}O$) and *carvene* which is a limonene ($C_{10}H_{16}$). 20. Oil of *Cloves* (*Oleum Caryophylli*, B.P.) and of *Pimento* (*Oleum Pimentæ*, B.P.), both heavier than water, consist of *eugenol* ($C_{10}H_{12}O_2$) and a sesquiterpene, $C_{15}H_{24}$ (*caryophyllene* in the case of oil of cloves, which contains also traces of vanillin). 21. Oil of *Cascarilla* (*Cascarilla*, B.P.) has not been fully examined. 22. Oil of *Cinnamon*-bark (*Cinnamomi Cortex*, B.P.) and of *Cassia*-bark is mostly cinnamic aldehyde (C_8H_7COH). It also contains eugenol and phellandrene. Boiled with nitric acid, it yields benzaldehyde, C_6H_5COH, and benzoic acid, C_6H_5COOH; with chlorinated lime it yields calcium benzoate, $(C_6H_5COO)_2Ca$; and with caustic potash it gives potassium cinnamate, C_8H_7COOK. The sp. gr. of oil of cinnamon (*Oleum Cinnamomi*, B.P.) varies from 1·025 to 1·035. 23. Oil of *Citronella*, a *Grass Oil*, from *Andropogon nardus*, is chiefly composed of *citronellal*, $C_{10}H_{18}O$. Kremers also obtains heptoic aldehyde, $C_7H_{14}O$, a terpene ($C_{10}H_{16}$), etc. 24. Oil of *Copaiba* (*Oleum Copaibæ*, B.P.) and, 25, of *Cubebs* (*Oleum Cubebæ*, B.P.) contain sesquiterpenes, $C_{15}H_{24}$. The *cubebene* of the latter oil is sometimes associated with *hydrous cubebene*, the so-called *cubeb camphor*, $C_{15}H_{25}OH$. Oil of cubebs also contains a small quantity of a terpene ($C_{10}H_{16}$). 26. Oil of *Coriander* (*Oleum Coriandri*, B.P.) consists of *coriandol*, $C_{10}H_{18}O$, and a terpene, $C_{10}H_{16}$. 27. The fruits of *Cumin* or *Cummin* (*Cuminum Cyminum*), an ingredient of many curry-powders, contain about 3 per cent., and those of *Water Hemlock* or *Cowbane* (*Cicuta virosa*) about 1¼ per cent., of an essential oil composed of *cymol* or *cymene*, $C_{10}H_{14}$, and *cuminic aldehyde*, $C_9H_{11}COH$. The latter is an aldehyde which readily unites with alkali-metal bisulphites and yields by oxidation *cuminic acid*, $C_9H_{11}COOH$. Cymol also occurs in *Garden Thyme* (*Thymus vulgaris*). 28. The fresh leaves of *Eucalyptus globulus*, *E. oleosa*, *E. cneorifolia*, *E. dumosa*, *E. odorata*, and other "mallee," "scrub," or shrub-like eucalypts, furnish about 1 per cent. of an oil (*Oleum Eucalypti*, B.P.), which contains from 40 to 60 per cent. of *cineol* or *eucalyptol*, $C_{10}H_{18}O$, boiling at about 174° C., freezing at 0° C., sp. gr. 0·927 together with pinene, $C_{10}H_{16}$. *E. amygdalina* yields an oil which contains little cineol and much phellandrene (the latter more readily alterable than other terpenes, and characterised by yielding a crystalline mass with nitrous anhydride). *E. maculata, var. citriodora,* contains an aldehyde similar to that of citronella. Different species of eucalyptus may yield oils differing in specific gravity, flavour, and odour. It is now generally accepted that the medicinal efficacy of eucalyptus oil is due to the cineol which it contains. Like the turpentines the eucalyptus oils are good solvents of resins. Their sp. gr. varies greatly—from 0·030 to 0·040 below or above 0·900. Voiry states that cineol is present also in the oil of *Lavandula spica,* oil of *spike* or "foreign" oil of lavender. *Red gum* (*Eucalypti Gummi,* B.P.) is from the bark of *E. rostrata* and other species, and is used solely for its astringent properties. A lozenge is official (*Trochiscus Eucalypti Gummi,* B.P.). 29. *Elecampane*-root (*Inula Helenium*) by distillation with water yields solid volatile *helenin* (C_6H_8O), *inulol,* a camphor-oil ($C_{10}H_{16}O$), and *inulic anhydride* or *lactone* ($C_{15}H_{20}O_2$), as well as, according to Marpmann, crystals of *alantic acid* ($C_{15}H_{22}O_3$) and fluid *alantol* ($C_{20}H_{32}O$) each more powerfully antiseptic than helenin. 30. Oil of *Fennel*-fruit (*Fœniculi Fructus,* B.P.) differs in odour, but contains the same proximate constituents as oil of anise. 31. Oil of *Geranium,* or *Ginger Grass* oil, from *Andropogon schœnanthus,* and various species of *Pelargonium,* contains *geraniol* ($C_{10}H_{18}O$). Barbier and Bouveault, however, give the name limonool to the essential oil of Andropogon schœnanthus, and state that it is different from oil of pelargonium. 32. *Grains of Paradise* (*Amomum melegueta*), Guinea Grains or Melegueta Pepper, *Semina Cardamomi Majoris,* contain essential oil ($C_{10}H_{16}$ and $C_{10}H_{16}O$) and a highly pungent principle, termed by Thresh *paradol,* $C_9H_{14}O_2$, isomeric with the capsaicin of the same chemist. 33. Oil of *American Pennyroyal* (*Hedeoma,* U.S.P., "the leaves and tops of *Hedeoma pulegioides*" contains *pulegone* ($C_{10}H_{18}O$), and yields *isoheptoic* acid ($C_7H_{14}O_2$), and other substances (Kremers). 34. Oil of *Juniper* (*Oleum Juniperi,* B.P.) contains pinene, $C_{10}H_{16}$, cadinene, $C_{15}H_{24}$, and a crystalline substance which has been called *juniper camphor.* 35. Oil of *Lavender* (*Oleum Lavandulæ,* B.P.) contains linalool, linalyl acetate, and a minute proportion of cineol; pinene, $C_{10}H_{16}$, is present in some samples, but is not a constant constituent. 36. Oil of *Myrcia* (*Oleum Myrciæ,* U.S.P.), oil of bay, or bayberry oil (sp. gr. 0·975 to 0·990) is obtained from the leaves of *Myrcia*

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* The student is not expected to remember, but to understand, all that follows respecting the volatile oils.

acris. It contains *eugenol* with some methyl-eugenol and small quantities of other substances. 37. Oil or butter or camphor of *Orris* (*Iris Florentina*) is a soft solid lighter than water. Flückiger and Hanbury found it to be chiefly myristic acid associated with a small quantity of essential oil. 38. Oil of *Peppermint* (*Oleum Menthæ Piperitæ,* B.P.) contains several hydrocarbons, $C_{10}H_{16}$, menthone, $C_{10}H_{18}O$, and other bodies, and deposits crystalline peppermint camphor known as menthol, $C_{10}H_{19}OH$, when exposed to low temperatures. The latter is official (*Menthol,* B.P., also *Emplastrum Menthol,* B.P.), and has the following characters: "In colourless acicular crystals, usually more or less moist from adhering oil; or in crystalline masses. Melting point 107·6° F. (42° C.); it should not exceed 109·4° F. (43° C.). It has the odour and flavour of peppermint, producing a sensation of warmth on the tongue, or, if air is inhaled, a sensation of coolness. It is very slightly soluble in water, but readily in alcohol (90 per cent.), the solutions having a neutral reaction. Boiled with sulphuric acid diluted with half its volume of water, Menthol acquires an indigo-blue or ultramarine colour, the acid becoming brown. It should be entirely volatilized by the heat of a water-bath." It is also yielded by the oil of *Mentha arvensis* (*vars. piperascens* and *glabra*). 39. *Pulsatilla,* U.S.P.:—Various species of *Anemone* and *Ranunculus* yield an acrid oil which with water gives poisonous crystalline *anemonin* ($C_{15}H_{12}O_6$) and amorphous *anemonic acid* ($C_{15}H_{14}O_7$). 40. Oil of *Spearmint* (*Oleum Menthæ Viridis,* B.P.), the common Mint of the kitchen garden, contains carvone, $C_{10}H_{14}O$, and a terpene. 41. Oil of *Pennyroyal* (*Mentha Pulegium*) consists chiefly of the ketone, pulegone ($C_{10}H_{18}O$). 42. Oil of *Nutmeg* (*Oleum Myristicæ,* B.P.) is composed of a hydrocarbon, *myristicene* ($C_{10}H_{16}$), and *myristicol* ($C_{10}H_{16}O$), and cymene ($C_{10}H_{14}$) (Gladstone). *Mace,* the arillus or net-like envelope of the nutmeg appears to yield similar bodies and also *myristicin,* $C_{12}H_{14}O_3$ (Semmler). 43. Oil or *Otto* or *Attar of Roses* (*Oleum Rosæ,* B.P.) contains citronellol ($C_{10}H_{19}OH$), geraniol ($C_{10}H_{17}OH$), and minute quantities of other constituents; the odour is not due to any single substance, but to the blending of geraniol and the other constituents. According to Flückiger, the solid hydrocarbon also present yields succinic acid as the chief product of its oxidation by nitric acid, and in other respects affords evidence of belonging to the paraffin series of fats. *Aqua Rosæ,* B.P., is prepared by distillation from the flowers of *Rosa damascena.* 44. Oil of *Rosemary-tops* (*Oleum Rosmarini,* B.P.) exists in the plant to the extent of from 1½ to 3 parts per 1000. It contains a hydrocarbon ($C_{10}H_{16}$) resembling that from Myrtle, *Myrtus communis,* also camphor ($C_{10}H_{16}O$) and borneol and cineol ($C_{10}H_{18}O$) in variable proportions. 45. Oil of *Rue* contains methyl-nonyl ketone, $C_{11}H_{22}O$ or $CH_3—CO—C_9H_{19}$ as chief constituent. Gorup-Besanez and Grimm have obtained artificial oil of rue ($C_{11}H_{22}O$), as one of the products of the destructive distillation of calcium acetate and caprate (*see* Ketones). According to Greville Williams oil of rue is chiefly euodic aldehyde ($C_{11}H_{22}O$), some lauric aldehyde ($C_{12}H_{24}O$) also being present. 46. Oil of *Sage* contains the hydrocarbon pinene, $C_{10}H_{16}$, along with thujone, $C_{10}H_{16}O$, and cineol and borneol, $C_{10}H_{18}O$. 47. Oil of *Savin,* obtained from the tops of *Juniperus Sabina,* contains sabinol, $C_{10}H_{16}O$, and sabinyl acetate. According to Wallach, it contains also a sesquiterpene, $C_{15}H_{24}$. 48. Oil of *Elder-flowers* (*Sambuci Flores,* B.P.) occurs in the flowers in very small quantity; it has a buttery consistence; it contains a terpene ($C_{10}H_{16}$), and probably a paraffin. 49. Oil of *Sandal-wood* (*Oleum Santali,* B.P.) is composed (Chapoteaut) of two substances: mostly of *santalal,* an aldehyde having the formula $C_{15}H_{24}O$ (boiling at 572° F., 300° C.), and a small quantity of the corresponding alcohol having the formula $C_{15}H_{26}O$ (boiling at 590° F., 310° C.). It occurs to the extent of about 2½ per cent. in the fragrant white or yellow sandal-wood of India, *Santalum album,* a small tree of the natural order Santalaceæ, and not to be confounded with the *Pterocarpus santalinus,* a tree of the natural order Leguminosæ, which furnishes the inodorous Red Sandal-wood or Red Sanders Wood or *Barwood* of the dyer. 50. Oil of *Sassafras-root* (*Sassafras Radix,* B.P.) contains nine-tenths of its weight of *Safrol* or *Sassafrol,* $C_{10}H_{10}O_2$, also *eugenol* and a small quantity of a terpene. Sassafras camphor, $C_{10}H_{16}O$, is deposited when the oil is exposed to a low temperature. 51. Oil of *Black Sassafras,* so-called, from "the dried bark of *Cinnamomum oliveri*" (*Oliveri Cortex,* Oliver Bark, B.P. Add. 1900) also contains safrol and eugenol as well as cineol and cinnamic aldehyde. 52. Oil of *Mustard* (*Oleum Sinapis Volatile,* B.P.) consists of allyl iso-thiocyanate, C_3H_5NCS, with small quantities of allyl cyanide, C_3H_5CN (*see* p. 494). If contaminated with alcohol, its sp. gr. is below 1·015. 53. Oil of *Sweet Flag* (*Acorus calamus*) contains a terpene, $C_{10}H_{16}$. (The rhizome is said to contain *Acorin*, $C_{36}H_{60}O_6$, a bitter glucoside.) 54. Oil of common garden *Thyme* (*Thymus vulgaris*) contains *cymene* or *cymol* ($C_{10}H_{14}$), *thymene* ($C_{10}H_{16}$), and *thymol* and *carvacrol* ($C_{10}H_{14}O$). *Thymol*, B.P., may be obtained from oil of *Thymus vulgaris*, *Monarda punctata*, or *Carum copticum*. Thymol crystallizes out when oil of thyme or of ptychotis, etc., is kept at a low temperature for a day or two. It may also be obtained by shaking the oils with caustic alkali, and treating the separated alkaline liquid with an acid. It may be purified by distillation, or by crystallization from alcohol. It would seem that as an antiseptic thymol is quite as valuable as carbolic acid. 55. Oil of *Turmeric* (*Curcuma longa*) is said by Jackson and Menke to be chiefly an alcohol having the formula $C_{19}H_{27}OH$. They name it *turmerol*. It is a light yellow volatile oil, having the sp. gr. 0·902. It is to this oil that turmeric (hence curry powder, partly) owes its flavour and odour. 56. Oil of *Valerian-root* (*Valerianæ Rhizoma*, B.P., from *Valeriana officinalis*) contains the two terpenes, camphene and pinene, $C_{10}H_{16}$, together with several borneol esters—formic, acetic, butyric, and, especially, iso-valerianic, A sesquiterpene, $C_{15}H_{24}$, and some other substances are also present. According to Bruylants, the strongly-smelling iso-valerianic acid does not exist free in the oil but is formed by the decomposition of the borneol ester. Iso-valerianic acid can rapidly be obtained from the rhizome by oxidation with a mixture of potassium bichromate and dilute sulphuric acid. The potassium salt is formed in quantity when oil of valerian is allowed to fall, drop by drop, on heated caustic potash, and by the action of sulphuric acid on the potassium salt thus produced, iso-valerianic acid is obtained. *Valeriana Wallichii* (*Valerianæ Indicæ Rhizoma*, B.P. Add. 1900) furnishes an Indian valerian oil resembling, in its general characters, the oil from *V. officinalis*. 57. Indian oil of *Verbena*, *Lemon-grass* Oil, or *Indian Melissa* Oil, is obtained from *Andropogon citratus* (*Oleum Graminis Citrati*, B.P. Add. 1900; *Oleum Andropogi Citrati*, P.I.). It consists mainly of citral associated with small quantities of an isomeric aldehyde and of citronellal. 58. Oil of *Ginger* (*Zingiber*, B.P.), is, according to Thresh, a complex mixture of hydrocarbons and their oxidation products; cymene ($C_{10}H_{14}$) is present, a terpene, aldehydes, and ethereal salts. 59. The oil obtained from the so-called *worm-seed* (*Artemisia maritima*) consists mainly of cineol ($C_{10}H_{18}O$). *American Wormseed* (*Chenopodium,* U.S.P.) contains a volatile oil.

Caoutchouc or *Indiarubber,* and *Gutta Percha.*

Caoutchouc is the hardened juice of *Dichopsis Gutta, Hevea* (*Siphonia*) *Brasiliensis, Castilloa elastica, Urceola elastica, Ficus elastica,* and other plants. Heated moderately with sulphur, it takes up 2 or 3 per cent., and forms *vulcanized indiarubber;* at a higher temperature a hard horny product, termed *ebonite,* or *vulcanite,* results. The official indiarubber (*Caoutchouc,* B.P.) is "the prepared milk-juice of Hevea brasiliensis, *Muell. Arg.* and probably other species." *Gutta Percha* is the concrete "drop" or juice of the *percha* (Malay) tree, *Isonandra gutta,* and of other Sapotaceous plants. White gutta percha is obtained by precipitating a solution of the ordinary gutta percha in chloroform by the addition of alcohol, washing the precipitate with alcohol, and finally boiling it in water and moulding it into the desired form while still hot. *Liquor Caoutchouc,* B.P., is a solution of indiarubber in benzol and carbon bisulphide, and takes the place of *Liquor Gutta Percha* (B.P. 1885) which was a solution of gutta percha in chloroform.

These two elastic substances, in the pure state, are hydrocarbons $(C_5H_4)_n$, usually slightly oxidized. When caoutchouc is distilled, a terpene, $C_{10}H_{16}$, called caoutchin, is obtained.

Camphors

In addition to the stearoptens or camphors already mentioned as being contained in or formed from volatile oils, there is one that is a common article of trade. It is obtained from the wood of *Cinnamomum Camphora,* or Camphor-laurel, in Japan (termed in Europe, Dutch camphor, because imported by the Dutch) and in China (known as Formosa camphor), by a rough process of distillation with water, and is resublimed in this country (*Camphora,* B.P.). The formula of laurel-camphor is $C_{10}H_{16}O$. Sp. gr. about 0·995; melting point, 175° C.; boiling point, 205° C. Bromine heated with camphor gives *monobrom-camphor* ($C_{10}H_{15}BrO$) and hydrobromic acid. Recrystallized monobrom-camphor occurs in white prisms. The essential oil, from which doubtless camphor is derived by oxidation, is easily obtained from the wood, and is occasionally met with in commerce under the name of *liquid camphor* or *camphor-oil.* It contains hydrocarbons resembling terebenthene and citrene, and hydrous camphor ($C_{10}H_{16}O$, H_2O) as well as camphor. By exposure to air it becomes oxidized and deposits common camphor. Camphor distilled with phosphoric anhydride yields cymene, $C_{10}H_{14}$. There is another kind of camphor, *Borneol,* in European markets, less common than laurel-camphor, but highly esteemed by the Chinese; it is obtained from *Dryobalanops aromatica,* and is denominated Sumatra or Borneo Camphor. It differs slightly from laurel-camphor in containing more hydrogen, its formula being $C_{10}H_{18}O$. It may be obtained by acting on camphor with hydrogen, the camphor being dissolved in some inert liquid such as toluene, and sodium added: the sodium forms a compound, $C_{10}H_{15}ONa$, while the hydrogen thus liberated acts on another portion of the camphor, forming borneol, $C_{10}H_{17}OH$—a better result being obtained if absolute alcohol is used instead of toluene (Jackson and Menke). Borneo camphor is accompanied in the tree by a volatile oil ($C_{10}H_{16}$) isomeric with oil of turpentine. This oil, *borneene,* is also occasionally met with in trade under the name of *liquid camphor* or *camphor-oil,* but differs from laurel-camphor oil in not depositing crystals on exposure to air.

The constitution of the camphors is still somewhat doubtful. Camphor is soluble to a slight extent in water, about 1 in 700. The Official Camphor Water (*Aqua Camphoræ,* B.P.) is such a solution.

Common camphor, and many other of the camphors, oily hydrocarbons, and oxidized hydrocarbons, yield *camphoric acid,* $C_8H_{14}(COOH)_2$, and camphoronic acid, $C_7H_9(OH)(COOH)_2$, when attacked by oxidizing agents. Such reactions indicate natural relationships. Camphoric acid is an antiseptic.

Cantharidin, $C_{10}H_{12}O_4$, the active blistering principle of cantharides (*Cantharis,* B.P.) and other vesicating insects (such as *Mylabris cichorii* or *Telini Fly,* P.I., *Mylabris phalerata,* and others—*Mylabris,* B.P. Add. 1900—common in India), has most of the properties of a camphor or a stearopten.

It slowly crystallizes from an alcoholic tincture of the beetles, in fusible, volatile, micaceous plates. The following process for the extraction of cantharidin is by Fumouze: Powdered cantharides are macerated with chloroform for twenty-four hours; and this treatment is repeated twice with fresh quantities of solvent, the residue having been well squeezed each time. The collected solutions are then distilled, and the dark-green residue treated with carbon bisulphide, which dissolves fatty, resinous, and other matters and precipitates the cantharidin. The precipitate is placed on a filter, washed with carbon bisulphide, and recrystallized from chloroform. Greenish and Wilson published a process for the quantitative determination of cantharidin in cantharides. (See *Pharmaceutical Journal*, vol. lx., p. 255.) The average amount found is six or seven parts in one thousand. Cantharidin is readily soluble in warm glacial acetic acid, and still more readily in acetic ether or chloroform. Cantharides from which the fat has been removed by petroleum ether yield their cantharidin with great facility.

Massing and Dragendorff consider cantharidin to be an anhydride, and that with the elements of water it forms *cantharidic acid* ($H_2C_{10}H_{12}O_5$). Piccard gives to cantharidin the formula $C_{10}H_{12}O_4$. Homolka assigns to it the formula $C_8H_{13}O_2CO{\cdot}COOH$.

Resins, Oleo-Resins, Gum-Resins

Resins seem to be products of the oxidation of terpenes and the allied hydrocarbons; they occur in plants, generally in association with volatile oils. They closely resemble camphors and stearoptens, but are not volatile, and differ from oils and fats chiefly in being solid and brittle. For convenience they are classified as resins, oleo-resins, and gum-resins, the distinctions being founded as much on physical as on chemical properties.

Oleo-resins are mixtures of a resin and a volatile oil.

Gum-resins are mixtures of a resin or oleo-resin and gum.

Balsams are commonly described as resins or oleo-resins which yield benzoic and cinnamic acids; they are Benzoin (*Benzoinum*, B.P.), Balsam of Peru (*Balsamum Peruvianum*, B.P.), Balsam of Tolu (*Balsamum Tolutanum*, B.P.), and Storax (*Styrax Præparatus*, B.P.), and are respectively treated of under the above-named acids.

Some oleo-resins, containing neither of the above acids, are often termed balsams (*e.g.*, balsam of copaiba, and Canada balsam); these are described under the head of Oleo-resins.

Resins.*—1. *Resin, rosin,* or *colophony* (*Resina,* B.P.), is the type of this class. Its source is the oleo-resin or true turpentine of the conifers, a substance which by distillation yields spirit of turpentine and a residuum of rosin. "Brown" and "white" resin are met with in trade. The former is the residue of American, the latter of Bordeaux turpentine (from *Pinus Abies,* etc., and *Pinus maritima* respectively). The chief constituents of brown resin are *pinic acid,* $HC_{20}H_{29}O_2$, and *sylvic acid,* identical in composition but differing in properties (*see* Isomerism), the former being soluble and the latter insoluble in cold alcohol (90 per cent.). White resin or "galipot" is chiefly *pimaric acid,* also isomeric with pinic acid. Pinic acid, cautiously heated, yields *colophonic* or *colopholic acid.* Resin, by destructive distillation, yields *resin oil,* the first portion being "pale," the next "blue," and the third "green" resin oil. Mixed with other oils, these oils are used for lubricating purposes and in the manufacture of printing ink. Among the products of the destructive distillation of resin, Tichborne found "*colophonic hydrate,*" $C_{10}H_{22}O_3, H_2O$, a white inodorous crystalline substance, and by depriving this of water obtained white crystalline *colophonin,* $C_{10}H_{22}O_3$. Resin is soluble in oil of turpentine. Contact with sulphuric acid immediately colours it strongly red. 2. *Arnicin,* $C_{20}H_{30}O_4$, the chief acrid, and one of the active, principles of the rootlets and rhizome of Arnica (*Arnicæ Rhizoma,* B.P.) and of the flowers (*Arnicæ Flores,* B.P. Add. 1900), is a resin, and, probably, a glucoside. 3. *Cannabin,* said to be the active principle of *Indian Hemp* (*Cannabis Indica,* B.P.), was obtained in 1846 by T. and H. Smith, and is a resin. According to Vignolo the essential oil of Cannabis Indica, purified by distillation in a current of steam and extraction with ether, is a mobile liquid boiling at 248°-268° C. After repeated distillation from metallic sodium in order to remove a stearopten, it yields a sesquiterpene, $C_{15}H_{24}$, as a mobile colourless oil of aromatic odour which boils at 256°, and has a density of 0·897 at 15·3° C., and is slightly lævo-rotatory. This soon resinifies on exposure to air, and on adding concentrated sulphuric acid to its chloroform solution the liquid becomes first green, then blue, and red on heating. Vignolo concludes that the "cannabene" prepared from this oil by Personne, was a mixture. Preobraschensky has stated, and since re-asserted, that the active principle is nicotine. Kennedy searched for nicotine by two methods, but found none. Hay found an alkaloid, *tetano-cannabine;* Siebold and Bradbury, also H. F. Smith, an alkaloid termed *cannabinine.* Warden and Waddell, after careful investigations, consider that the active principle of the plant has yet to be isolated. Jahns finds choline present. The native names of Indian hemp, that is, of the cultivated "dried flowering or fruiting tops of the female plants of *Cannabis sativa,*" are *ganga* and *gunjah.* It is chiefly grown in Bengal. *Guaza* is the name of the Bombay product which includes the wild plant. Both are used for smoking, and form the equivalent of the tobacco of western nations. *Bhang,* or *sidee,* consists of the dried leaves, fruit, and twigs of the wild plant. Its infusion is used as a beverage, as tea is in Europe and elsewhere. *Hashish,* made from bhang, corresponds to *Extractum Cannabis Indicæ,* B.P. *Charas* or *churras* is a resinous exudation of the plant, and is also used for smoking. All these preparations are stimulating and narcotic. 4. *Capsicum-fruit* contains a resin (p. 553). 5. *Castorin,* a resinous matter, is the name given to the chief constituent of *Castor,* the dried preputial follicles and included secretion of the Beaver (*Castor Fiber*). 6. *Copal.*—The best copal is the exuded resin of trees of extinct forests, and is found beneath the surface of the ground in the neighbourhood of existing trees. It appears to be a mixture of acids, but its character is still obscure. Experiments by Wallach and Rheindorff show that when copal is distilled, and the oily distillate washed with soda and distilled with steam, a mobile liquid boiling at 40°-350° C. is obtained. The lowest boiling portions of this liquid seem to contain isoprene; the portions boiling at 151°-164° consist principally of a hydrocarbon of the composition $C_{10}H_{16}$, which was proved to be pinene, and the fractions boiling at about 175° were found to contain dipentene. 7. *Doundaké-bark,* an African febrifuge, from *Sarcocephalus esculentus,* owes its activity to resinoid substances, according to Heckel and Schlagdenhauffen. 8. *Dragon's Blood* is a crimson-red resin found as an exudation on the mature fruits of a Rotang or Rattan Palm (*Calamus draco*). According to Dieterich it contains a large proportion of aromatic esters, with *dracoalban*, $C_{20}H_{40}O_4$, *dracoresen*, $C_{26}H_{44}O_2$, and other substances. 9. *Ergotin* is a very active resinoid constituent of *Ergot* (*Ergota*, B.P.), *i.e.*, the sclerotium (compact mycelium or spawn) of *Claviceps purpurea*, originating in the ovary of the common rye, *Secale cereale*. According to Wenzell, ergot contains two alkaloids, *ecboline* and *ergotine*, to the former of which, he says, the activity of ergot is due. Blumberg considers these alkaloids to be identical. Tanret states that an unstable alkaloid termed *ergotinine* occurs in ergot to the extent of 1 per 1000 and that it is accompanied by a camphor; also *ergosterin*, $C_{26}H_{40}O$, H_2O, resembling cholesterin. Dragendorff and Podwissotzki assert that ergot owes most of its activity to *sclerotic* or *sclerotinic acid*, present to the extent of about 4 per cent. Recent investigations seem to show that *cornutine* is an active alkaloid of ergot, associated with ergotinic and sphacelinic acids, picrosclerotine and ergotinine. The activity really seems to be due to a combination of alkaloids and acids, and not to any one constituent, as no principle representing the full activity of ergot has been extracted. Ergot also contains *choline*, which by decomposition may yield trimethylamine. "*Ergotin*" (*Extractum Ergotæ*, B.P.) is obtained from ergot by extraction with alcohol (60 per cent.), and purification of the product. 10. *Guaiacum-resin* (*see* p. 582). 11. *Jalap-resin* (*see* p. 583). 12. *Kousso* (*Cusso*, B.P.) yields yellow crystals of a resinoid substance readily soluble in alkaline liquids, *kosin* or *koussin*, $C_{31}H_{38}O_{10}$. It is, perhaps, an anhydride. 13. *Mastic* is a resinous exudation obtained by incision from the stem of the Mastic or Lentisk tree. Nearly nine-tenths of mastic is *mastichic acid*, $C_{20}H_{32}O_3$, a resin soluble in alcohol; the remainder consists of *masticin*, $C_{20}H_{32}O$, a tenacious elastic resin, and a terpene having the formula $C_{10}H_{16}$. 14. *Mezereon*, the dried bark (*Mezerei Cortex*, B.P.) of *Daphne Mezereum*, Mezereon, *Daphne laureola*, Spurge Laurel, and of *Daphne Gnidium*, owes its acridity to a resin. 15. *Pepper* contains resin (*see* p. 628). 16. *Burgundy pitch* (*Pix Burgundica*, B.P.) is the melted and strained exudation from the stem of the Spruce Fir, *Picea excelsa*. The term Burgundy is a misnomer, the resin never having been collected in or near Burgundy; Finland, and to a small extent, Baden, and Austria being the countries whence it is derived. Its constituents closely resemble those of ordinary resin. It is often adulterated and imitated by a mixture of resin with palm-oil, water, etc., from which it may readily be distinguished by its duller yellow colour, highly aromatic odour, greater solubility in alcohol, and almost complete solubility in twice its weight of glacial acetic acid (Hanbury). 17. *Podophyllum-resin.*—In preparing the resin of podophyllum or May-apple (*Podophylli Resina,* B.P.; *Podophylli Indicæ Resina,* B.P. Add. 1900), an alcoholic extract of the rhizome and rootlets (*Podophylli Rhizoma,* B.P., from *Podophyllum peltatum; Podophylli Indicæ Rhizoma,* from *Podophyllum emodi*) is poured into acidulated water; the resin is then deposited. According to Guareschi, podophyllum contains a glucoside resembling convolvulin. Podwissotzki has extracted from podophyllum a small quantity of crystalline colouring matter, fat, a bitter crystalline acid, a bitter crystalline neutral principle, and an amorphous acid resin. Kürsten states that the latter yields a crystalline active substance, *podophyllotoxin,* $C_{23}H_{24}O_9$ (Dunstan and Henry, $C_{15}H_{14}O_6$) which seems to be the active principle both of *Podophyllum peltatum,* the American drug (official in B.P.) and *P. emodi,* the Indian plant. 18. *Pyrethrin* is the acrid resinous active principle of the root of *Anacyclus pyrethrum* or *Pellitory-root* (*Pyrethri Radix,* B.P.). According to Buchheim, alkalies break it up into piperidine and pyrethric acid. The crystalline poisonous principle obtained by Bellesme from *Pyrethrum carneum,* the powder of which (and *P. roseum,* and especially *P. cinerariæfolium,* or Dalmatian Insect Powder) is the well-known "insecticide," has not yet been analysed. 19. The resins of Rhubarb. (*See* Chrysophanic Acid.) 20. *Rottlerin,* $C_{33}H_{30}O_9$, is the crystalline resin from Kamala, the minute glands that cover the capsules of *Rottlera tinctoria:* to this and, apparently, allied resins (*isorottlerin,* A. G. Perkin) Kamala owes its activity as an anthelmintic.

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* The student is not expected to remember, but to understand all that follows respecting the resins.

Oleo-resins.—1. "*Capsicin,*" a term suggestive of a definite chemical substance, is a name somewhat unhappily accorded to an indefinite substance, an oleo-resin, obtained by digesting the alcoholic extract of Capsicum fruit (*Capsici Fructus,* B.P.) in ether and evaporating the clear ethereal fluid to dryness. Besides volatile oil and resin, capsicum fruits contain much fatty matter which Thresh states is chiefly free palmitic acid. (*See* also *Capsicine* and *Capsaicin*, p. 620). 2. *Copaiba* (*Copaiba*, B.P.) is a mixture of essential oil ($C_{15}H_{24}$), *copaivaöl*, $C_{20}H_{32}$ (Strauss), with 2 or more per cent. of brown soft resin, and 30 to 60 per cent. of a yellow dark resin consisting mostly of *copaivic acid*, $C_{20}H_{32}O_2$, with *oxycopaivic acid*, $C_{20}H_{28}O_3$ (Fuhling), and *metacopaivic acid*, $C_{22}H_{34}O_4$ (Strauss). Copaiba, containing about equal parts of this acid and of the oil, heated with a fourth of its weight of the official magnesium carbonate, yields a transparent fluid, owing to the formation of magnesium copaivate and solution of this soap in the essential oil. With an equal weight of the carbonate, enough soap is produced to take up the whole of the essential oil, and form a mass capable of being rolled into pills. A much smaller quantity of calcined magnesia, as might be expected, effects the same result; but more time, often several days, is required before the interaction is complete. Quicklime has a similar effect. Copaiba, unlike 3, *Wood-oil* or *Gurjun Balsam* (*Dipterocarpi Balsamum*, P.I.), a similar oleo-resin from *Dipterocarpus turbinatus* (*D. Lævis*, P.I.) is almost entirely soluble in absolute alcohol and in petroleum spirit. Copaiba is often slightly fluorescent; Gurjun balsam is highly fluorescent. The stated analogy of Gurjun balsam to copaiba is borne out by its chemical composition; for by distillation it yields about 40 per cent. of an essential oil identical in composition with oil of copaiba, the non-volatile portion being resinous. The adulteration of copaiba with fixed oil is best detected by heating 20 or 30 drops in a capsule until all essential oil has evaporated. (Turpentine is betrayed by its odour during this evaporation.) The residue, copaiba resin, is brittle if pure, and more or less sticky or soft if fixed oil is present. 4. Oleo-resin of cubebs, an ethereal extract of cubebs decanted from waxy matter, was formerly official. 5. *Elemi* is an exudation from a tree growing in the Philippine Islands. It consists of volatile oil ($C_{10}H_{16}$) with 80 or more per cent. of two resins, the one ($C_{20}H_{32}O_2$) soluble in cold alcohol, the other, *Amyrin*, $(C_5H_8)_5,H_2O$, almost insoluble, associated with *Amyric acid* $(C_5H_8)_7O_4$ (Buri). There is an α- and a β-amyrin, each having the formula $C_{30}H_{49}OH$ (Vesterberg). It also contains small quantities of two crystalline bodies soluble in water, *Bryoidin*, $(C_5H_8)_4,3H_2O$, and *Breidin* (Flückiger). The

Icacin of Stenhouse and Groves is either identical with amyrin, or perhaps has the formula $(C_5H_8)_9,H_2O$. All these substances are probably hydrous terpenes. 6. *Wood-tar* (*Pix Liquida,* B.P.) is a mixture of several resinoid and oily substances (amongst others Creosote, *see* p. 502) obtained by destructive distillation from the wood of *Pinus sylvestris* and other pines. When heated, it yields a terebinthinate oil (*Oleum Picis Liquidæ,* U.S.P.) and a residue of *pitch.* (*Earth Pitch* or *Asphalte,* appears to be a partially oxidized petroleum.) *Oleum Cadinum,* B.P., "*Huile de Cade,*" or *Juniper Tar Oil,* is the product of the similar destructive distillation of *Juniperus Oxycedrus.* 7. *Turpentines.*—These oleo-resins have been mentioned in connection with *oil of turpentine,* their volatile constituent, and *resin,* their fixed constituent. 8. *Common Frankincense* (*Thus Americanum,* B.P.) is the concrete turpentine of *Pinus palustris* and *Pinus tæda.* 9. *Canada Balsam* (*Terebinthina Canadensis,* B.P.) is largely gathered in the province of Quebec, and is the turpentine or oleo-resin of the Balm of Gilead Fir (*Abies balsamea*). 10. *Sumbul-root* (*Sumbul Radix,* B.P.) contains 9 per cent. of resin, to which probably it owes its stimulating properties. The resin consists of two parts, one soluble in ether and the other in alcohol, together with valerianic, sumbulic, and sumbuolic acids. By dry distillation it yields a blue oil. 11. *Oleo-Resin of Lupulin* (U.S.P.) is an ethereal extract of the yellow glandular powder (*Lupulinum,* B.P.) attached to the small nuts at the base of the scales which form the aggregate fruit of the Hop (*Humulus Lupulus*). It contains a volatile oil which is chiefly composed of a sesquiterpene, an oxidized oil or resin, a bitter extract containing the hop-bitter, lupulinic acid, $C_{25}H_{36}O_4$, and tannic acid. It generally contains a good deal of earthy dust, but should not yield more than 12 per cent. of ash, and not more than 40 per cent. of matter insoluble in ether.

GUM-RESINS.—1. *Ammoniacum* (*Ammoniacum,* B.P.) is an exudation from *Dorema Ammoniacum.* It contains 20 per cent. of gum, a little volatile oil, and 70 per cent. of resin ($C_{40}H_{50}O_9$—Johnston). 2. *Asafetida* (*Asafetida,* B.P.) is a gum-resin obtained, by incision, from the living root of *Ferula fœtida.* It contains from 50 to 70 per cent. of a resin which is partly *ferulaic acid,* $C_{10}H_{10}O_4$, 25 to 30 per cent. of gum (about two-thirds arabin, one-third bassorin, p. 573), a little vanillin, and 3 to 5 per cent. of volatile oil, which (Semmler) contains two sulphur compounds, $C_7H_{14}S_2$, and $C_{11}H_{20}S_2$, two terpenes, $C_{10}H_{16}$, and a sesquiterpene, $C_{15}H_{24}$. 3. *Euphorbium,* an old drug which is an emetic and purgative gum-resin, contains an amorphous active resin, crystalline *euphorbon,* $C_{15}H_{24}O$, and other substances. 4. The ordinary or Siam *Gamboge* (*Cambogia,* B.P.) of European trade is obtained from the *Garcinia Hanburii;* the gamboge of India (*Cambogia Indica,* B.P. Add. 1900, and P.I.) from *G. morella.* When of best quality, it contains about 20 per cent. of a gum, and 75 to 80 per cent. of a yellow resin termed *gambogic acid,* $C_{20}H_{24}O_4$. 5. *Galbanum* (*Galbanum,* B.P.) consists of about 25 per cent. of gum, about 65 per cent. of resin, and 9 or 10 per cent. of volatile oil. Moistened with alcohol, and then with hydrochloric acid, some varieties of galbanum yield a purple colour. Galbanum heated for some time to 212° F. (100° C.) with hydrochloric acid, the liquid separated and shaken with ether or chloroform, and the latter evaporated, yields somewhat less than 1 per cent. of colourless acicular crystals of *umbelliferone,* $C_9H_6O_3$. According to Flückiger and Hanbury, umbelliferone is soluble in water; its solution exhibits, especially on addition of an alkali, a brilliant blue fluorescence which is destroyed by an acid. A small fragment of galbanum immersed in water, shows fluorescence on the addition of a drop of ammonia. The same phenomenon occurs with asafetida, and slightly with ammoniacum; it is probably due to traces of umbelliferone pre-existing in these drugs. Umbelliferone is also produced from many other aromatic umbelliferous plants, as *Angelica, Levisticum* (Lovage, the basis of an old cordial or liqueur), and *Meum,* when their respective resins are submitted to dry distillation; also from the resin of *Daphne mezereum.* The fluorescence of umbelliferone may be shown by dipping bibulous paper into water which has stood for an hour or two on lumps of galbanum, and drying it. A strip of this paper placed in a test-tube of water with a drop of ammonia will give a superb blue solution, instantly losing its colour on the addition of a drop of hydrochloric acid. 6. *Myrrh* (*Myrrha,* B.P.), an exudation from the stem of *Balsamodendron Myrrha,* contains about half its weight of soluble arabinoid gum, 10 per cent. of insoluble gum (probably bassorin), 2½ of volatile oil, isomeric with thymol and carvone (Köhler), and about 25 per cent. of resin (myrrhic acid). 7. *Olibanum* (P.I.), or *Thus masculum,* or *Arabian Frankincense* (from various species of *Boswellia*) is about one-third gum and nearly two-thirds resin ($C_{40}H_{30}O_6$), with a little hydrocarbon ($C_{10}H_{16}$) and oxidized hydrocarbon volatile oils. It has always been an important ingredient of *incense*—myrrh, storax, benzoin, and such fragrant combustible resinous substances, being other constituents. 8. *Scammony* (*see* p. 587).

Gum-resins need only to be finely powdered and rubbed in a mortar with water to yield a medicinal *emulsion*, in which the fine particles of resin are held in suspension by the aqueous solution of gum.

QUESTIONS AND EXERCISES

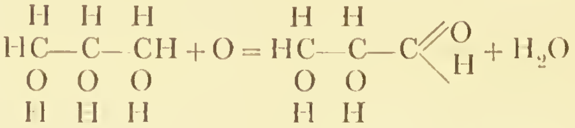
What are the general chemical characters of volatile oils?—How do volatile oils usually differ chemically from fixed oils?—Describe the usual process by which volatile oils are obtained.—How does natural turpentine differ from turpentine of trade?—With what object is commercial turpentine rectified?—What is the chemical nature of indiarubber and gutta percha?—How is indiarubber *vulcanized* and converted into *ebonite* or *vulcanite?*—Mention the difference in composition between the volatile oils of *Anthemis nobilis* and *Matricaria Chamomilla.*—Give the systematic name for oil of horse-radish.—State the general composition of the oils of lemon, lime, bergamot, citron, and cedra.—Name the constituents of oil of cloves.—In what respect does otto of roses differ from other oils?—What class of substances forms the chief part of oil of rue?—How is camphor-oil related to camphor?—In what respects do Borneo or Sumatra camphor and camphor-oil differ from the corresponding products of Japan and China?—How may Borneol be artificially prepared?—How do resins occur in nature? Distinguish between resins and camphors. Mention the points of difference of resins, oleo-resins, gum-resins, and balsams. —Name the sources of common resin or rosin.—Enumerate some official articles of which the active constituents are resins.—Give the distinguishing characters of Burgundy pitch.—What is the average proportion of oil and of resin in the so-called balsam of copaiba?—Explain the effect of magnesium carbonate, magnesia, and lime on copaiba.—Why do ammoniacum, asafetida, gamboge, galbanum, myrrh, and similar substances give an emulsion by mere trituration with water?

CARBOHYDRATES

Under the name *carbohydrates* there are grouped a large number of compounds containing carbon with hydrogen and oxygen in the same proportion as in water. They include sugars, dextrin, starch, cellulose, etc. The molecules of some of these are very complex, but are resolved by hydrolysis into sugars such as glucose.

The most commonly occurring carbohydrates contain six or multiples of six carbon atoms; but analogous substances with three, five, seven, eight, or nine carbon atoms in the molecule are also known.

The sugars are amongst the simplest of the carbohydrates. A large number of them, some identical with previously known natural sugars, some previously unknown, have been synthesized. They are partially oxidized polyhydric alcohols, having one of their alcohol groupings oxidized into an aldehyde or ketone group. For example, the trihydric alcohol glycerin, on oxidation with bromine in presence of solution of sodium carbonate, yields *glycerose,* which has all the characters of a sugar.



$$\begin{array}{ccccccc} \mathrm{H} & \mathrm{H} & \mathrm{H} & & \mathrm{H} & \mathrm{H} & \\ \mathrm{HC}- & \mathrm{C}- & \mathrm{CH} & + \mathrm{O} = & \mathrm{HC}- & \mathrm{C}- & \mathrm{C}\begin{smallmatrix} /\!\!/ \mathrm{O} \\ \diagdown \mathrm{H} \end{smallmatrix} + \mathrm{H_2O} \\ \mathrm{O} & \mathrm{O} & \mathrm{O} & & \mathrm{O} & \mathrm{O} & \\ \mathrm{H} & \mathrm{H} & \mathrm{H} & & \mathrm{H} & \mathrm{H} & \end{array}$$

This, however, is not stable, but spontaneously condenses into a glucose, $C_6H_{12}O_6$.

Erythrose, $C_4H_8O_4$, is an example of a sugar with four, and *arabinose,* $C_5H_{10}O_5$, of one with five, atoms of carbon. Most of the natural sugars are glucoses ($C_6H_{12}O_6$) or compounds of two or three molecules of glucose minus water (*bioses* or *trioses*).

Sugars with seven, eight, and nine atoms of carbon have been constructed by treating glucoses with hydrocyanic acid, which combines with the aldehyde or ketone group to form the nitrile of an acid containing one more carbon atom. This on hydrolysis gives the acid, the lactone (*see* p. 585) of which may be reduced in acid solution to the corresponding sugar by the action of sodium amalgam. This process is then repeated to get an eight-carbon sugar, and so on. One of these seven-carbon sugars was found to be identical with a natural sugar, *perseite,* but most of them have not yet been found occurring naturally.

Glucoses, $C_6H_{12}O_6$

Glucoses, $C_6H_{12}O_6$. There are two chief types of these six-carbon sugars, differing from each other in the position of the alcohol grouping that has undergone oxidation, and classed accordingly as aldehyde and ketone sugars—*aldoses* and *ketoses.* *Ordinary glucose,* or *dextrose* is an example of the first class, and *fructose* or *lævulose* of the second. Each of these classes contains a very large number of physical isomers, differing from each other in their action on polarized light and in some other respects; these may be most readily distinguished from one another by means of the physical characters of the compounds they form with phenyl-hydrazine (*see* p. 593). The large number of these isomers is accounted for, on the stereo-chemical theory, by the circumstance that there are no fewer than four asymmetrical carbon atoms (*see* p. 348) in each molecule. Thus there are three dextroses, dextro-rotatory, lævo-rotatory, and inactive; three analogous mannoses; three fructoses or lævuloses, etc.

All the glucoses above mentioned have been obtained artificially, the starting-point being an artificial glucose (*acrose,* $C_6H_{12}O_6$) obtained by the condensation of formaldehyde—$6CH_2O = C_6H_{12}O_6$; it is probably in a similiar way that natural sugars are produced by plants.

Glucose (from γλυκὺς, *glucūs,* sweet), or *Grape-sugar,* or *Dextrose* is often seen in the crystallized state in dried grapes or raisins and other fruits; the sugar of diabetic urine, also, is one of the many glucoses. Its crystalline character is quite distinct from that of cane-sugar, the latter forming short monoclinic prisms, while grape-sugar occurs in masses of small six-sided plates. Grape-sugar is also less soluble in water, but more soluble in alcohol than cane-sugar.

According to Fresenius, the percentage proportion of saccharine matter in the dried fig is 60 to 70, grape 10 to 20, cherry 11, mulberry 9, currant 6, whortleberry 6, strawberry 6, raspberry 4.

Fructose, or *Fruit-sugar,* or *Lævulose* is the uncrystallizable, or very difficultly crystallizable, constituent of "inverted" (*see* p. 560) cane-sugar. It is found in the grape, fig (*Ficus,* B.P.), cherry, gooseberry, strawberry, peach, plum and other fruits, often with dextrose or with cane-sugar. Fruit-sugar reduces cupric salts and silver ammonio-nitrate.

Ordinary fructose is lævo-rotatory, while sucrose and ordinary glucose are dextro-rotatory; the latter rotate a ray of polarized light to the right and the extent of the rotation varies with the amount of sugar present—a fact easy of application in determining the amount of sugar present in syrups or in diabetic urine.

Artificial formation of Grape-sugar from Cane-sugar. Test for sugar.—Dissolve a grain or two of cane-sugar in water. To a portion of this solution placed in a test-tube add more water, two or three drops of solution of cupric sulphate, a considerable quantity of solution of caustic potash or soda (enough to turn the colour of the liquid from a light to a dark blue), and heat the mixture to the boiling-point; no obvious immediate change occurs. To another portion of the sugar solution add a drop of sulphuric acid, and boil for ten to twenty minutes, then add the cupric solution and alkali, and heat as before; a yellowish-red precipitate of cuprous oxide, Cu_2O, is produced. This test is exceedingly delicate.

The above reaction is due to the conversion of the *cane-sugar*, $C_{12}H_{22}O_{11}$, into *inverted sugar*,* a mixture of glucose and fructose, by the influence of the sulphuric acid, and to the reducing action of the glucose and fructose on the cupric solution. The formation of a precipitate immediately, without the action of acid, shows the presence of the latter sugars —its formation only after ebullition with acid indicating, in the absence of starch or dextrin, cane-sugar. In this reduction-process the sugar is oxidized and broken up into several substances; but the exact nature of the reaction has not been ascertained.

Dextrin also reduces the cupric salt to cuprous oxide, unless its solution is cold and very dilute. It does not however, so act on a solution of cupric acetate acidified with acetic acid, while glucose produces with this liquid the usual red cuprous precipitate (Barfoed).

Sugar from Starch.—Boil starch with a small quantity of water and a drop of sulphuric acid as in the preparation of dextrin, but continue the ebullition for several minutes; on testing a portion of the cooled liquid with iodine, and another portion with the heated alkaline solution of a cupric salt, as just described, it will be found that the starch has nearly all become converted into a sugar—glucose. Maltose is also formed, at first, but by the continued action of the acid is changed to glucose. When made on a large scale, a warm (131° F., 51° C.) mixture of starch and water, of the consistence of cream, is slowly poured into a boiling solution of one part of sulphuric acid in one hundred of water, the whole boiled for some time, the acid neutralized by adding chalk, the mixture filtered, the liquid evaporated to a thick syrup and set aside; in a few days it crystallizes to a mass resembling solidified honey. In this operation a small quantity of dextrin remains with the glucose; but if the process be conducted under pressure, conversion, according to Manbré, is complete. Sugar made from the starch of rice, maize, etc., is largely used for table syrups, confectionery, bee food, and as a partial substitute for malt in brewing. It is known as *patent sugar, saccharine, maltose,* etc.

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* The name *inverted sugar* originated from the fact that while a solution of cane-sugar rotates the plane of polarization of light to the right, the sense of the rotation is reversed, or "inverted," when cane-sugar is hydrolysed into glucose and fructose. Although the glucose so obtained is right-rotating and is equal in quantity to the fructose, yet the latter possesses left-rotating power to such an extent as to predominate over the right-rotation of the glucose, and a left-rotating mixture results.

In the United States the dealers term the syrups "glucose," and the further evaporated solid product "grape-sugar." The former contain one-third or more of glucose, about one-fifth of maltose, one-fourth or more of dextrin, and about one-sixth or one-fifth of water; the latter often contain about three-fourths of glucose, from none up to one-third of maltose, and one-seventh or one-sixth of water.

Galactose (from milk-sugar), *Sorbinose* (from mountain-ash berries), *Inosite* (from muscle), *Mannose* (from mannite), *Gulose, Formose, β-Acrose, Dambose* (from a caoutchouc), and *Scyllite* (from many fish), are other glucoses.

Saccharoses, or Bioses, $C_{12}H_{22}O_{11}$

Cane-sugar, or *Sucrose* (*Saccharum Purificatum,* B.P.), is a frequent constituent of vegetable juices. Thus it forms the chief portion of cassia pulp (*Cassiæ Pulpa,* B.P.), is contained in the carrot and turnip, but is most plentiful in the sugar-cane; much, however, is now obtained from the sugar-maple and beetroot. On evaporation of the juice, common *brown* or *moist sugar* crystallizes out; this by re-solution, filtration through animal charcoal, evaporation to a highly concentrated syrup, and crystallization in moulds, yields the compact crystalline conical loaves known in the trade as *loaf-sugar.* These loaves when broken into fragments or sawn into cubes form *lump-* or *cube-sugar.* From a slightly less concentrated syrup, slowly cooled, the crystals termed *sugar-candy* are deposited, white or coloured, according to the colour of the syrup. The official syrup (*Syrupus,* B.P.) is an aqueous solution, consisting of two-thirds sugar and one-third water.

The sugar in fresh fruits is mainly cane-sugar; but by the action of the acid, or possibly of a ferment in the juice, it is gradually converted into a mixture of glucose and fructose in varying proportions. Ripe Hips contain 30 per cent. of such sugar, besides gum and acid malates and citrates. Sugar from flowers, as gathered in the form of syrup by bees, is probably a mixture of these two varieties. It is gradually altered to a crystalline or granular mass consisting largely of glucose, as seen in dried fruits, such as Raisins and the Prune (*Prunum,* B.P.), and in solidified Honey. Honey often contains pollen, hairs, spores, the dust from the flowers, and various flocculent matters which cause it to ferment and yield mannite, alcohol, and acetic acid; hence for use in medicine it is directed that honey be clarified by melting and straining while hot through flannel previously moistened with warm water (*Mel Depuratum,* B.P.). A mixture of clarified honey 80 per cent., acetic acid 10 per cent., and water 10 per cent., is official under the name of *Oxymel* (from ὀξὺς, *oxus,* acid, and μέλι, *meli,* honey). A similar mixture of honey with acetic acid containing the soluble portions of squill-bulbs (*Scilla,* B.P.) is known as Oxymel of Squill (*Oxymel Scillæ,* B.P.). Such a mixture, also, made from the younger bulbs of *Urginea indica* and of *Scilla indica* (*Urginea,* B.P. Add. 1900) forms *Oxymel Urgineæ* (B.P. Add. 1900). Honey and cane-sugar are the bases of the official *Confections.*

Maltose, $C_{12}H_{22}O_{11}$.—This crystallizable sugar is formed, together with dextrin, when diastase or dilute acids act upon starch. In the case of diastase it is the ultimate product, but the dilute acids may convert it into glucose. It differs also from glucose in its optical activity.

Cane-sugar, maltose, and grape-sugar yield alcohol and carbonic anhydride by fermentation, the cane-sugar and the maltose apparently undergoing hydrolysis before the production of alcohol commences.

In *bread-making*, some of the starch is converted into dextrin, and this into sugar by the ferment. The above action then goes on, the liberation of gas producing the *rising* or swelling of the mixture of flour, water, and yeast (dough). The temperature to which the mass is subjected in the oven causes the escape of most of the alcohol, and the expansion of the bubbles of carbonic anhydride in every part of the now spongy loaf. The carbonic anhydride gradually evolved when flour is worked up for bread with a mixture of dry sodium bicarbonate and tartaric acid (best preserved by previous admixture with dried flour and a little magnesium carbonate)—*baking-powder*—exerts similar influence. The least objectionable method of introducing carbonic anhydride, however, is that of Dauglish, whose patent aërated bread is made from flour by admixture with carbonic acid water under pressure by the aid of machinery. On removal from the cylinder, the resulting dough expands by the natural elasticity of the imprisoned carbonic anhydride, and the oven completes the process. All fermented bread retains, obviously, a little alcohol, sometimes 0·25 per cent.

Action of Alkali on Sugar.—To a solution of grape-sugar add solution of caustic potash or soda, or solution of potassium carbonate, and warm the mixture; the liquid is darkened in colour from amber to brown, according to the amount of grape-sugar present. A very little picric acid greatly intensifies the colour.

Tests.—The above, the copper-reaction, and the fermentation process (p. 485) form three good tests for the presence of grape-sugar, and, indirectly, of cane-sugar. A piece of merino or other woollen material, previously dipped in a solution of stannic chloride and dried, becomes of a brown or black colour when dipped in a solution of glucose and heated to about 300° F. (about 150° C.) by holding before a ire.

Barley-sugar is made by heating cane-sugar with water until the whole is liquefied and then boiling off the added water, a change from the crystalline to the vitreous condition occurring, with absorption of heat. The greater portion of confectioners' "sweets" are formed of vitreous sugar. They slowly revert to the crystalline condition, with evolution of heat. *Treacle, Molasses* or *Melasses* (from *Mel,* honey), or *Golden Syrup,* chiefly results from the application of too much heat in evaporating the syrups of the sugar-cane; it is a mixture of cane-sugar with uncrystallizable sugar and more or less colouring matter. Liquorice-root (*Glycyrrhizæ Radix,* B.P.) contains much uncrystallizable sugar.

Caramel.—Heat a grain or two of sugar in a test-tube until it blackens and froths; the product is *caramel,* or *burnt sugar* (the *Saccharum Ustum* of pharmacy). It is used as a colouring agent for gravies, confectionery, spirits, vinegar, and similar materials. It is a mixture of substances, "caramels" having slightly varying properties.

Milk-sugar, or *Lactose,* $C_{12}H_{22}O_{11},H_2O$ (*Saccharum Lactis,* B.P.), the sweet principle of the milk of animals, is not susceptible of alcoholic fermentation by ordinary yeast; certain species of *saccharomyces,* however, convert it into alcohol. It resembles grape-sugar in reducing an alkaline cupric solution with precipitation of cuprous oxide. It is obtained from milk by adding a few drops of acid, stirring, setting aside for the *curds* to separate, filtering, evaporating the *whey* to a small bulk, filtering again if necessary, and allowing to cool and crystallize. The deposited crude "*sugar*-sand" is afterwards refined and recrystallized. Thus obtained, milk-sugar has the formula above given, but if deposited from the hot solution during evaporation, the crystals are anhydrous, $C_{12}H_{22}O_{11}$. Milk-sugar is convertible by the action of dilute acids (hydrolysis) into galactose and glucose; these may be made to interact to form milk-sugar. Powdered milk-sugar is used in pharmacy as a vehicle for potent solid medicines. The official article is "in crystals or in crystalline masses, greyish-white, hard, odourless, faintly sweet. Soluble in 7 parts of cold water, and in about 1 part of boiling water. It should not leave more than 0·25 per cent. of ash when incinerated with free access of air." A limit of ash is necessary as a test of purity, because magnesium carbonate or oxide, if added to neutralize the acidity of the whey during evaporation, as is sometimes done, gives rise to the presence of magnesium lactate in the milk-sugar, and this salt being converted into carbonate or oxide on incineration, increases the amount of ash.

Saccharic Acid, $H_2C_6H_8O_8$, or $C_4H_4(OH)_4(COOH)_2$, is the product of the oxidation of sucrose, glucose, starch, gum, and lignin by nitric acid. Mannose yields *manno-saccharic acid,* isomeric with saccharic acid. *Mucic acid,* also isomeric with saccharic acid, may be obtained by the oxidation of lactose, gum, and dulcite.

Melitose or *Melitriose* (from eucalyptus) is a triose, giving on hydrolysis galactose, glucose, and fructose. *Melezitose* (from the larch) and *Trehalose* (from Turkish manna), belong to the Saccharoses.

"*Honey-dew*" is a viscid saccharine matter occasionally met with on the leaves of the lime, maple, black alder, rose, and other trees, being a sweet principle exuded from aphides. Sometimes it is sufficiently abundant to dry and fall on the ground, forming a veritable "shower of manna." It is a mixture of cane-sugar, inverted sugar, and dextrin.

QUESTIONS AND EXERCISES

Into what three classes may the carbohydrates be divided?—How is grape-sugar obtained from cane-sugar?—How are cane-sugar and grape-sugar analytically distinguished?—How is dextrose obtained from starch?—Mention the chief sources of cane-sugar.—Give chemical explanations of the processes of bread-making.—What is the difference between fruit-sugar and honey?—What is oxymel?—Describe the effect of heat on cane-sugar.—How is milk-sugar obtained, and how does it differ from other sugars?—How may mucic and saccharic acids be obtained?

Amyloses, or Amyloids, $nC_6H_{10}O_5$

Starch, $nC_6H_{10}O_5$, is contained in large or small quantities in nearly every plant. It forms about 60 to 70 per cent. of wheat, and from 20 to 30 per cent. of potatoes. The starch officially recognised in the British Pharmacopœia (*Amylum*) may be that of wheat (*Triticum sativum*); maize (*Zea Mays*), and rice (*Oryza sativa*).

Experiment.—Rasp or grate, or scrape with a knife, a portion of a clean raw potato, letting the pulp fall on to a piece of muslin placed over a small dish or test-glass, and then pour a slow stream of water over the pulp; minute particles or *granules* pass through the muslin and sink to the bottom of the vessel, fibrous matter remaining on the sieve. The granules consist of potato starch. Even diseased potatoes furnish good starch by this method. Wheat-starch may be obtained by tying up some flour in a piece of calico, and kneading the bag in a slow stream of water flowing from a tap, the washings running into a deep vessel, at the bottom of which the starch collects; the sticky matter remaining in the bag is *gluten.*

The *blue starch* of the shops is artificially coloured with smalt or indigo, to neutralize the yellow tint of recently washed linen; it should not be used for medicinal purposes. Starch dried in mass splits up into the familiar columnar masses in which the commercial article is met with.

Gluten is the substance which gives tenacity to dough and bread. It seems to be a mixture of vegetable fibrin, vegetable casein, and an albuminous matter termed glutin. Each of these bodies contains about 16 per cent. of nitrogen. In the anhydrous condition gluten consists of carbon 52·6 per cent., hydrogen 7 per cent., nitrogen 16 per cent., and oxygen, with a trace of sulphur, 24·4 per cent. *Wheaten Flour* contains about 72 per cent. of starch and 11 of gluten, as well as sugar, gum, fine bran, water, and ash. The compactness of barley, well seen in *Husked* or *Pearl Barley,* is said to be due to the large amount of vegetable fibrin present. During germination the fibrin is destroyed; hence, probably, the cretaceous character of malt. *Oatmeal,* popular when made into "porridge," is rich in albumenoids, or flesh-forming constituents, containing nearly 16 per cent. *Sago* is granulated starch from the Sago Palm; *tapioca* from the Bitter Cassava: each has less than 1 per cent. of albumenoids. The white translucent *Rice* grains are the husked seeds of *Oryza sativa.* Rice is a staple article of food in tropical countries. Ground rice (*Oryzæ Farina*), resembles flour of wheat in composition, but contains from 85 to 90 per cent. of starch.

Mucilage of Starch.—Mix two or three grains of starch with first a little and then more water, and heat to the boiling point; starch mucilage (*Mucilage of Starch*, B.P.) results.

This mucilage or paste is not a true solution; by long boiling, however, a portion of the starch becomes dissolved. In the latter case the starch probably becomes somewhat altered.

Test.—To some of the mucilage add a very little free iodine; a deep-blue colour is produced. This reaction is a very delicate test for the presence of either iodine or starch. The starch must be in the state of mucilage; hence in testing for starch the substance supposed to contain it must first be boiled with water. The solutions used in the reaction should also be cold, or nearly so, as the blue colour disappears on heating, though it is partially restored on cooling. The iodine reagent may be iodine-water or tincture of iodine. In testing for iodine, its occurrence in the free state must be ensured by acidulation if necessary, and the addition of a drop, or even less, of chlorine-water. Excess of chlorine must be avoided, or iodic acid will be formed, which does not colour starch.

The so-called *iodide of starch* scarcely merits the name of a chemical compound, the state of union of its constituents being so feeble that it is decomposed at 100° F. (37·7° C.), while substances which attack free iodine remove that element from it. Thus the alkalies, hydrogen sulphide, sulphurous acid and other reducing agents, destroy the blue colour. Dry starch will absorb, according to its source, from 6 to 8 per cent. of iodine; but in the state of mucilage three times the quantity. There are probably three definite compounds of starch with iodine. With nitric acid, starch yields an explosive compound (*Xyloïdin*) $C_{12}H_{16}O_6(NO_3)_4$. Two isomeric tetranitro-derivatives, as well as a penta- and a hexanitro-derivative, are known.

Composition of Starch Granules.—Starch granules consist mainly of *granulose*, soluble in cold water and giving an indigo colour with iodine, and *starch cellulose,* insoluble in water and giving with iodine a dirty yellow colour, with, possibly, other carbohydrates. The starch cellulose forms an external coating upon the granule, and also exists mixed with the granulose inside the granule. If this coating be broken by mechanical means, the continued application of cold water removes all the granulose, leaving the cellulose insoluble. By the action of diastase, ptyalin, and other ferments, and by other means, the granulose may be converted into sugar and dextrin, leaving the starch cellulose unacted upon.

Microscopic Examination of Starches.

All kinds of starch afford the blue colour with iodine, showing their chemical similarity. Physically, however, the granules of different starches differ from each other; hence a careful microscopic examination of any starch, or of any powder or vegetable tissue containing starch, enables the observer to state, with a high degree of probability, the source of the starch, either at once if he has much experience, or after comparing the granules in question with authentic specimens. A glance at the accompanying eight engravings * of common starches will show to what extent different starch granules differ naturally in size, shape, general appearance, distinctness and character of the *rugæ,* and position of the more or less central point or *hilum.* While from different starches individual granules may be picked out which much resemble each other, the appearance of each starch as a whole is fairly characteristic; that is to say, each *group* of granules differs in one or more characters from similar *groups* of granules of other starches.

A quarter-inch object-glass will commonly suffice for the microscopic examination of starch. A very little of the starch is mixed on a glass slide with a drop of water, and a piece of thin covering-glass placed on the drop and gently pressed, so as to provide a very thin layer for observation. Instead of water, diluted alcohol, diluted glycerin, turpentine or other essential oil, Canada balsam, and other fluids

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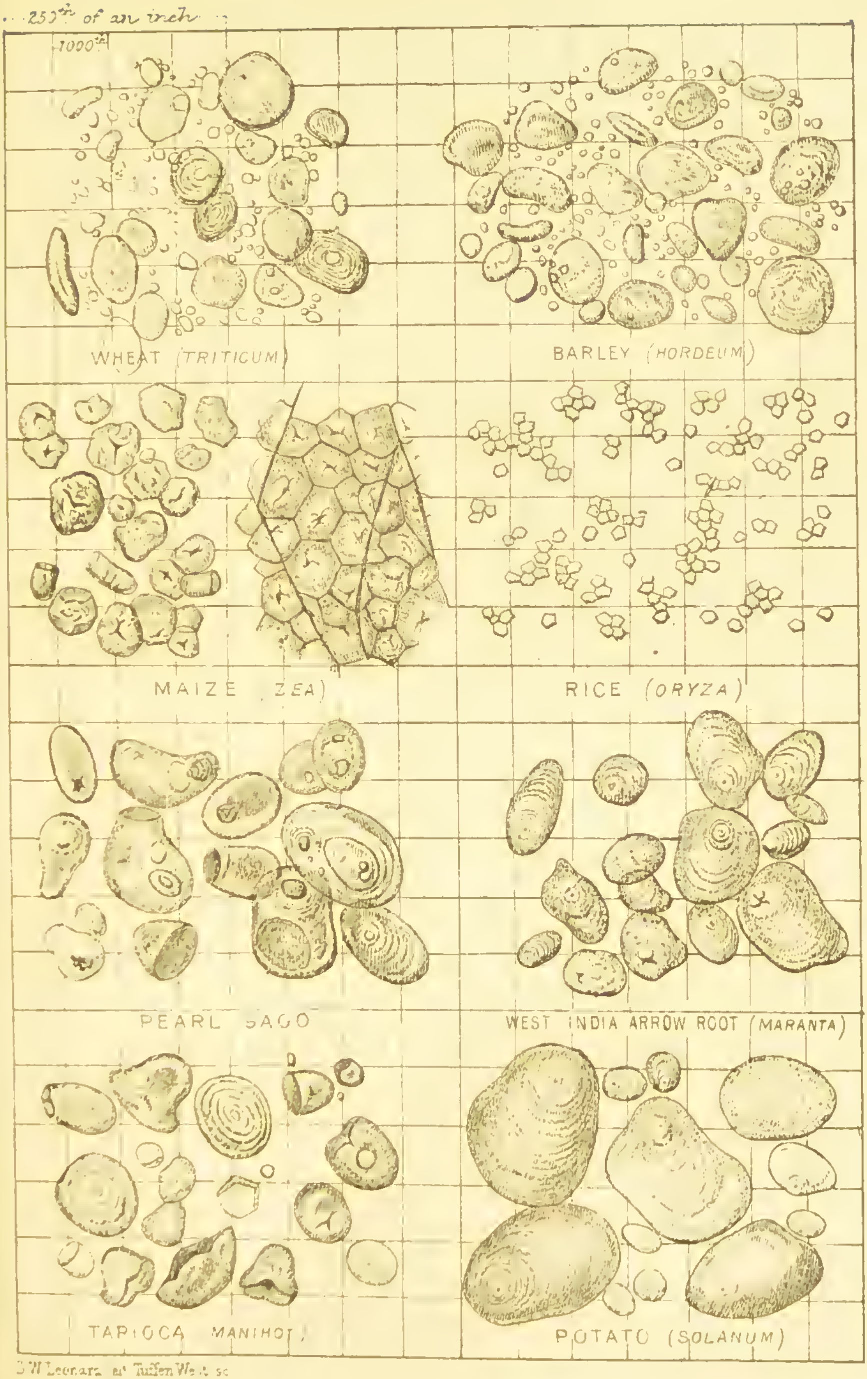
* By permission of Messrs Longmans & Co., these engravings have been copied, with very few modifications, from the plates in two of the three volumes of the original edition of Pereira's "Materia Medica."

STARCHES

mag^{d} 250 dia^{s}



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may be used in cases where the markings or other appearances are not well defined. The illumination also of the granules may be varied, the light being reflected or transmitted, concentrated or diffused, white or coloured, polarized or plain. Polarized light is especially valuable in developing differences, and in intensifying the effects of obscure markings. By polarized light the granules of potato starch appear as if traversed by a black cross; wheat starch granules and many others also peculiarly and characteristically influence polarized light. Distinctive characters will sometimes present themselves only when the granules are made to roll over in the fluid in which they have been temporarily mounted, or when the slide is gently warmed. Starches which have already been subjected to the influence of heat, partly, as in sago or tapioca, or almost entirely, as in bread, will of course differ in appearance from granules of the same starch before being dried, cooked, or torrefied. The characters of a starch will also vary somewhat according to the age and condition of the plant yielding it.

The description of the microscopic characters of the official varieties of starch* is as follows:—1. Wheat starch: A mixture of large and small granules, the former lenticular in shape, and marked with faint concentric striæ surrounding a nearly central hilum. 2. Maize starch: Granules more uniform in size, frequently polygonal, somewhat smaller than the large granules of wheat starch, and having a very distinct hilum but no evident concentric striæ. 3. Rice starch: Granules extremely minute, nearly uniform in size, polygonal, and without evident hilum or striæ.

The student may place fair confidence in the accompanying lithographs, and in most of the published engravings of starch-granules; but in microscopic analyses of importance the worker should, if possible, himself obtain actual specimens of starches for comparison from the respective seeds, fruits, and other tissues.

Inulin, $6C_6H_{10}O_5,H_2O$ (Kiliani), occurs with similar substances, *pseudo-inulin*, $16C_6H_{10}O_5,H_2O$, and *inulenin*, $10C_6H_{10}O_5$,

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* For plates and descriptions of the characters of other starches occurring in plants used for medicinal purposes, the reader is referred to works on Materia Medica, and to the indexes of Journals of Pharmacy, as well as to general works and magazines on microscopy. For engravings of starch granules *in situ*, *see* Berg's "Anatomischer Atlas," published by Gaertner, Berlin.

$2H_2O$ (Tanret). It is a white powder apparently occupying the place of starch in the roots of many plants, especially those of the natural order *Compositæ*. Twenty to forty-five per cent. has been obtained from elecampane (*Inula helenium*). It is also contained in the dahlia, colchicum, arnica, dandelion, chicory, artichoke, etc. It is soluble in boiling water, nearly all being re-deposited on cooling. Iodine turns it yellow. Long ebullition converts it into a kind of gum. Like starch, inulin is convertible into sugar, but by its own special ferment, the existence of which in the Jerusalem Artichoke has been demonstrated by J. R. Green. This ferment differs from diastase in being without the power of converting starch into sugar.

Lichenin, $nC_6H_{10}O_5$, is a white starch-like powder largely contained in many lichens—Iceland "Moss," *Cetraria Islandica*, and many others. It is soluble in boiling water, and the fluid gelatinizes on cooling. It may be precipitated from its aqueous solution by addition of alcohol. With iodine it gives a reddish-blue colour.

Glycogen, or *animal starch*, is the name given to the solid matter stored in the liver and resulting from the dehydration of the digested hydrated food which has been carried to the liver by the portal vein.

Dextrin, $nC_6H_{10}O_5$.—Mix a few grains of starch with half a test-tubeful of cold water and a drop or two of sulphuric acid, and boil for a few minutes; no thick mucilage is formed, and the liquid, if sufficiently boiled, yields, on cooling, no blue colour with iodine; the starch has become converted into *dextrin* and sugar. Dextrin is also produced if starch is maintained at a temperature of about 320° F. (160° C.) for a short time. Dextrin is largely manufactured in the latter way, and a paste of it is used by calico printers as a vehicle for colours; it is termed *British gum*. The change may also be effected by *diastase*, a peculiar ferment existing in malt. Mix two equal quantities of starch with equal amounts of water, adding to one a little ground malt, then heat both slowly to the boiling-point: the mixture without malt, thickens to a paste; that with malt remains thin, its starch having become converted into dextrin and maltose.

Diastase is probably a mixture, but possibly an oxidation product, of the coagulable albumenoids. It is so named from *διάστασις* (*diastasis*), *separation*, in allusion to the separation, or rather alteration, it effects among the constituent atoms of the molecule of starch. This function is shared by the saliva, pancreatic juice, bile, and the intestinal and other juices. The function is completely destroyed when the albumenoids are coagulated by a temperature of from 176° to 178° F. (80° to 81° C.).

The action of diastase upon starch.—Diastase has scarcely any action upon unbroken starch granules. The granules must be ruptured by gelatinization with heat and moisture, or in some other way. When a solution containing diastase, such as a cold water-infusion of malt, is allowed to act upon gelatinous starch or starch-paste at 140° to 160° F. (60° to 71° C.), liquefaction occurs. It is possible to operate so that when liquefaction has taken place, the solution shall give no reaction for sugar or dextrin. If this solution be concentrated and allowed to cool, a glistening white precipitate of soluble starch falls. Soluble starch is probably the result of the partial decomposition of the more complex molecule of granulose or gelatinous starch. The next step in the action of diastase upon gelatinous starch is the breaking down of the soluble starch molecule into dextrin and maltose. At least ten dextrins are successively produced, each simpler than the one preceding it, the proportion of maltose being correspondingly increased. The dextrins first produced give a red or brown colour with iodine, while those last produced, and having a simpler molecule, give no colour with iodine. The final reaction may be expressed thus:—

$$\underset{\text{Soluble starch}}{10(C_{12}H_{20}O_{10})} + 8H_2O = \underset{\text{Maltose}}{8(C_{12}H_{22}O_{11})} + \underset{\text{Dextrin}}{4(C_6H_{10}O_5)}$$

The dextrins are distinguished by their rotatory power, their reducing action on cupric salts, and in other ways.

Starch heated with glycerin is converted into the soluble variety. The latter may be precipitated from an aqueous solution by strong alcohol. A concentrated solution in water gradually gelatinizes, owing to reconversion into insoluble starch (Zulkowsky).

The action of dilute acids upon starch.—Dilute acids act upon gelatinous starch in the same way as diastase, except that the final product is glucose.

Malt (the word malt is said to be derived from the Welsh *mall*, soft or "rotten") is simply barley which has been softened by steeping in water, and allowed to germinate slightly, any further change being then arrested by the application of heat in a kiln. During germination the gluten breaks up and yields a glutinous substance termed vegetable gelatin, diastase, and other matters. To the vegetable gelatin is due much of the "body" of well malted and slightly hopped beer; it is precipitated by tannic acid; hence the thinness of ale (pale or bitter) brewed with a large proportion of hops or other material containing tannic acid. A portion of the diastase reacting on the starch of the barley converts it into dextrin, and, indeed, carries conversion to the further stage of maltose, as will be explained immediately. The temperature to which the malt is heated is made to vary, so that the sugar of the malt may or may not be partially altered to a dark-brown colouring material; if the temperature is high, the malt is said to be *high-dried*, and is used in porter-brewing; if low, the product is of lighter colour, and is used for ale. The diastase remaining in malt is still capable of converting a large quantity of starch into dextrin and maltose; hence the makers or distillers of the various spirits operate on a mixture of malted and unmalted grain in preparing liquors for fermentation.

Extract of Malt is an evaporated infusion of malt. Taken with food, its diastase aids in the conversion of starch into maltose and dextrin, and, *pro tanto*, assists enfeebled digestive powers.

$$\underset{\text{Starch}}{3C_6H_{10}O_5} + H_2O = \underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + \underset{\text{Dextrin}}{C_6H_{10}O_5}$$

As diastase begins to lose this power at temperatures above 150° F. (55·5° C.), that limit should not be exceeded in evaporating the infusion; indeed, if the dissolved albumenoid matters are to be retained, the evaporation should be conducted at 120° F. (48·8° C.).

The following method serves for the determination of the diastasic power of malt extract:—1·5 grammes of extract are dissolved in 15 c.c. of water and mixed with a mucilage of 0·1 gramme of starch in 100 c.c. of water. The mixture is raised to 140° F. (60° C.) and tested from time to time by adding two drops of iodine solution to 5 c.c. of it, and comparing with 5 c.c. of a similar mixture to which no starch has been added. If the two solutions do not exhibit any difference of tint this indicates the completion of the reaction. Good malt extract will accomplish this within half an hour, some samples will take less time, but many commercial extracts will require three hours or more.

Gum is a frequent constituent of vegetable juices, existing in large quantity in several species of Acacia. The nature of gums is very little known, though most probably they all belong to the carbohydrates. According to Fremy, gum contains a calcium salt (sometimes also a potassium salt) of the *gummic* or *arabic* radical, though consisting mostly of arabin or arabic acid alone. The formula of gummic acid is said to be $H_2C_{12}H_{18}O_{10},H_2O$, but from the important researches of O'Sullivan, it would seem to be far more complex, a multiple of the empirical formula $C_6H_{10}O_5$—according to Raoult $(C_6H_{10}O_5)_7$. Gum differs from dextrin in yielding mucic acid when oxidized by nitric acid. Good adhesive mucilages may be made from such gum-arabic substitutes as "ghatti," "amrad," etc. *Indian Gum* (*Gummi Indicum*, B.P. Add. 1900) is an exudation from the wood of *Anogeissus latifolia*. It has double the mucilaginous strength of Gum Acacia. *Cerasin* or cherry-tree gum is calcium metagummate, an insoluble modification of acacia gum. *Bassorin, tragauthin,* or *adraganthin*, $C_{12}H_{20}O_{10}$, is a form of gum which is insoluble in water, but absorbs large quantities of that liquid and forms a jelly-like mass: it occurs largely in Tragacanth, combined, like arabin, with calcium. *Pectin,* or Vegetable Jelly, $C_{32}H_{40}O_{28}$, $4H_2O$, is the body which gives to expressed vegetable juices the property of gelatinizing: it forms the chief constituent of Irish or Carrageen "Moss" (*Chondrus crispus*). *Ceylon "Moss"* (*Gracillaria lichenoides* and *G. conferroides*, P.I.) contains from one-third to three-fourths of vegetable jelly. Many seaweeds yield a jelly when a decoction of them is cooled. The Japanese freeze the jelly of *Gelidium corneum* and then cut it into strips; these slowly dried form the so-called *Japanese isinglass, Chinese Moss,* or *gelose* of Payen. It is probably a carbohydrate. With water, it is said to give a jelly 10 times stronger than that obtained from gelatin.

The mucilage of marsh-mallow root (*Althea officinalis*) and of linseed or common flax-seed (*Linum usitatissimum*) is a gum-like substance containing much mineral matter. It is the basis of the infusions termed *mallow-tea* and *linseed-tea*. Somewhat similar mucilage occurs in Bael Fruit (*Belæ Fructus*, B.P. Add. 1900), the fresh half-ripe fruit of *Ægle Marmelos*. It is also largely yielded by the seeds of the Quince (*Pyrus Cydonia*). *Salep*, the powdered dried tubers of many species of *Orchis*, contains a large quantity of such matter, as also does *Squill*. The Indian *Okra* (*Hibisci Capsulæ*, P.I., from *Hibiscus esculentus*) and *Ispaghul* or *Spogel* seeds (*Ispaghulæ semina*, P.I.; *Ispaghula*, B.P. Add. 1900; *Plantago ovata*, Forsk., *Plantago Ispaghula*, Roxb.) also appear to contain a considerable quantity.

Cellulin, or *cellulose*, $n\text{C}_6\text{H}_{10}\text{O}_5$, the woody fibre of plants, familiar, in the nearly pure state, under the forms of "cotton wool" (*Gossypium*, B.P., hairs of the seed of various species of Gossypium), paper, linen, and pith, is another substance isomeric, probably polymeric, with starch. Lignin is a closely allied body, lining the interior of the woody cells and vessels of plants. By the action of nitric acid of various degrees of concentration on cellulin, di-, or tri-nitrocellulins, and possibly others, are readily formed:—$n\text{C}_6\text{H}_8\text{O}_3(\text{NO}_3)_2$; $n\text{C}_6\text{H}_7\text{O}_2(\text{NO}_3)_3$. Trinitrocellulin is highly explosive gun-cotton; dinitrocellulin is not sufficiently explosive for use instead of gunpowder. Mononitrocellulin has not been so thoroughly examined as the others, but is said to be scarcely at all explosive; its formula is $n\text{C}_6\text{H}_9\text{O}_4\text{NO}_3$. The heat of a water-bath may explode trinitrocellulin, but not dinitrocellulin if pure. The three displaceable hydroxyl groups in cellulin may be displaced by groups other than the nitric radical.

Dinitrocellulin (*Pyroxylinum*, B.P.) may be prepared by the following official process:—Mix 5 fluid ounces of sulphuric acid and 5 of nitric in a porcelain mortar, immerse 1 ounce of cotton-wool in the mixture, and stir it for three minutes with a glass rod, so that it is thoroughly and uniformly wetted by the acids. Transfer the cotton to a vessel containing a considerable volume of water, stir it rapidly and well with a glass rod, decant the liquid, pour more water upon the mass, agitate again, and repeat the affusion, agitation, and decantation until the washings no longer give a precipitate with barium chloride. Drain the product on filter-paper, and dry on a water-bath.

Pyroxylin may also be made by soaking 7 parts of white filter-paper, which has been washed in hydrochloric acid and dried, in a mixture of 140 parts of sulphuric acid (sp. gr. 1·82) and 70 of nitric acid (1·37) for three hours, and well washing the product (Guichard).

Trinitrocellulin or gun-cotton is insoluble in a mixture of alcohol and ether; *dinitrocellulin* or *pyroxylin* is soluble, the solution forming ordinary collodion (*Collodium*, B.P.). The official proportions are 1 ounce of pyroxylin dissolved in a mixture of 36 fluid ounces of ether and 12 of alcohol (90 per cent.). After digesting for a few days, decant the liquid from any sediment and preserve it in a well-corked bottle. It dries rapidly upon exposure to air, and leaves a thin transparent film, insoluble in water or alcohol. *Flexible collodion* (*Collodium Flexile*, B.P.) is a mixture of collodion (48 fluid parts), Canada balsam (2 parts), and castor oil (1 part). *Blistering Collodion* (*Collodium Vesicans*, B.P.) is a solution of pyroxylin in acetic ether containing the active blistering principle of cantharides. Many articles of utility and beauty are now made of pyroxylin variously coloured and sold under the name of *xylonite* (*ξύλον, xulon,* wood) or *celluloid*.

Tunicin, or animal cellulose, exists in the mantle of *Ascidia*.

QUESTIONS AND EXERCISES

How is wheat-starch or potato-starch isolated?—Define gluten and glutin.—Enumerate the proximate principles of wheaten flour.—Is starch soluble in water?—Which is the best chemical test for starch?—Distinguish physically between the varieties of starch.—Into what compound is starch converted by heat?—What occurs when a mixture of starch and water is allowed to flow into hot dilute sulphuric acid?—Describe the different results of heating starch with water alone, and with water and a small quantity of ground malt.—Write a short article on the chemistry of malting.—What is the nature of gum arabic, and how is it distinguished from "British gum"?—Mention the properties of the products of the action of nitric acid of various degrees of concentration on cellulin.—How is pyroxylin prepared?

GLUCOSIDES

Source.—The glucosides are certain vegetable principles which, by ebullition with dilute acid, or by other treatment, take up the elements of water (*i.e.*, undergo hydrolysis) and yield glucose, accompanied by a second substance, which differs in each case according to the glucoside operated on. Some of the glucosides may be regenerated from the substances into which they are converted by hydrolysis. Tannin, which has already been described among the acids, is held by some authorities to be a glucoside.

Note on Nomenclature.—The first portion of the names of glucosides and neutral principles generally is commonly given in allusion to origin; the last syllable is *in*.

The following paragraphs deal with the glucosides and with a few other non-alkaloidal vegetable principles which are of pharmaceutical interest and importance.

ABSINTHIN, $C_{15}H_{20}O_4$, the bitter principle of *Artemisia Absinthium*, or *wormwood*, yields, when boiled with acids, glucose, volatile oil and a resin of the aromatic series. (The liqueur termed *absinthe* is ethyl alcohol (of varying strength) flavoured with natural oil of wormwood, coloured by chlorophyll, and slightly sweetened.)

AMYGDALIN, $C_{20}H_{27}NO_{11},3H_2O$. This substance, obtained by Robiquet and Boutron-Charlard in 1830, was the first discovered glucoside (Liebig and Wöhler, 1837). It is a white crystalline substance, existing in the bitter almond (*Amygdala Amara*, B.P.) but not in the sweet (*Amygdala Dulcis*, B.P.). About 2 per cent. is readily extracted by strong alcohol from the cake left when the fixed oil has been expressed from bitter almonds. From the concentrated alcoholic solution ether precipitates the amygdalin.

Experiment.—Make an emulsion of two or three sweet almonds by bruising and rubbing them with water, and notice that it has no odour of essential oil of bitter almonds; add a grain or two of amygdalin: an odour of essential oil of bitter almonds is at once developed. Bruise two or three bitter almonds and rub with water: the volatile oil is again developed.

The source of the benzaldehyde, or essential oil of bitter almonds, in these reactions, is the amygdalin, which, under the influence of *synaptase* or *emulsin* (a nitrogenous, casein-like ferment existing in bitter and sweet almonds), splits up into benzaldehyde, hydrocyanic acid, and glucose :—

$$\underset{\text{Amygdalin}}{C_{20}H_{27}NO_{11}} + \underset{\text{Water}}{2H_2O} = \underset{\text{Benzaldehyde}}{C_6H_5COH} + \underset{\text{Hydrocyanic acid}}{HCN} + \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

As each molecule of amygdalin yields one of hydrocyanic acid, a simple calculation shows that 17 grains (mixed with emulsion of sweet almonds) will be required to form one grain of hydrocyanic acid, a quantity equivalent to 55 minims of the diluted hydrocyanic acid of the British Pharmacopœia. The hydrocyanic acid is probably in chemical combination with the oil, to the extent of about 5 per cent. According to Lindo, the production of the benzaldehyde is preceded by the formation of benzaldehyde-cyanhydrin, $C_6H_5CH(OH)CN$. The emulsin and amygdalin occur in different parts of the bitter almond. *Aqua Amygdalæ Amaræ*, U.S.P., is made from the essential oil, which therefore is also included in the U.S.P.

Test.—The reaction between synaptase and amygdalin is applicable as a test for the presence of one by the addition of the other, even when mixed with much organic matter.

When amygdalin is warmed with fuming hydrochloric acid, mandelic, or phenylglycollic acid, $C_6H_5{\cdot}CHOH{\cdot}COOH$, is produced.

Cherry Laurel Water (*Aqua Laurocerasi*, B.P., by distillation with water from *Laurocerasi Folia*, B.P.) contains hydrocyanic acid derived from a reaction similar to, indeed probably identical with, that described above, for bitter almond oil is simultaneously produced. But the proportion of amygdalin or analogous substance in cherry-laurel leaves is most variable; hence the quantity of hydrocyanic acid in the distillate is variable. The British Pharmacopœia, however, directs that it shall contain 0·1 per cent. of real hydrocyanic acid, it being strengthened by the addition of hydrocyanic acid, or, if necessary, diluted by the addition of distilled water, until it has the prescribed strength.

Linseed yields a glucoside, *linamarin*, related to amygdalin, for it affords glucose and hydrocyanic acid on hydrolysis.

Pruni Virginianæ Cortex.—This, the recently dried bark of *Prunus serotina,* furnishes by distillation an essential oil and hydrocyanic acid as also do the seeds of the Quince (*Pyrus Cydonia*). The Wild Black Cherry, collected in autumn, contains amygdalin.

Caution.—Essential oil of almonds is of course highly poisonous. The purified oil or benzaldehyde is almost innocuous; it is obtained on distilling the crude oil with milk of lime and ferrous chloride, and drying the product by shaking with fused calcium chloride. The so-called "artificial oil of bitter almonds" or nitrobenzene, $C_6H_5NO_2$, when taken in quantity, has been known to produce death. The presence of nitrobenzene in oil of bitter almonds is detected by adding a little of the oil to a mixture of zinc and dilute sulphuric acid, shaking well, setting aside for an hour or two, filtering off the clear liquid, which now contains phenylamine, or aniline, and adding some potassium chlorate; a violet colour is produced, due to the oxidation of the aniline with formation of aniline mauve (*see* p. 650). Or the specimen may be shaken with sodium bisulphite to fix the benzaldehyde (for all such aldehydes form a compound with sodium bisulphite), and then with ether, which dissolves out, and on evaporation will yield, the nitrobenzene.

Arbutin, $C_{12}H_{16}O_7$, and *methyl-arbutin,* $C_{13}H_{18}O_7$, are contained in the leaves of *Arctostaphylos Uva Ursi, Chimaphila umbellata* and many ericaceous plants. Arbutin is a neutral substance occurring in acicular crystals, and resolvable by acids into *hydroquinone,* $C_6H_6O_2$, and glucose, and by gentle oxidation into *quinone,* $C_6H_4O_2$, and formic acid. *Ericolin,* $C_{34}H_{56}O_{21}$, is another bitter glucoside in bear-berry leaves.

Cathartic Acid.—The name cathartic acid was given by Dragendorff and Kubly to the glucoside-acid to which the purgative properties of Alexandrian Senna (*Senna Alexandrina,* B.P.) and of Tinnevelly Senna (*Senna Indica,* B.P.) appear to be chiefly due. Genz states that the formula for the acid is $C_{30}H_{36}NO_{15}$. The acid itself, which is obtained in the form of a black mass, is described as insoluble in water, alcohol, and ether, while its alkali-metal and other salts which occur in senna are readily soluble. Dilute alkalies dissolve it, yielding solutions from which it is reprecipitated on adding an acid. Its ammonium salts give brownish flocculent precipitates with salts of silver, tin, mercury, copper, and lead.

When boiled with dilute acids, cathartic acid undergoes hydrolysis, yielding cathartogenic acid and glucose.

Buckthorn Juice (*Rhamni Succus,* B.P., 1867) owes its cathartic properties to a substance apparently identical with cathartic acid.

Colocynthin, $C_{56}H_{84}O_{23}$.—This substance is the active bitter and purgative principle of colocynth-fruit (*Colocynthidis Pulpa,* B.P.): it is soluble in water and alcohol, but not in ether. By ebullition with acids it furnishes glucose and a resinoid substance.

Convolvulin.—*See* Jalapin.

Cotoin, $C_{14}H_{12}O_4$, appears to be the chief active principle of Coto bark, a Bolivian remedy for diarrhœa. A similar bark, *false coto,* or *paracoto,* contains *paracotoin,* $C_{12}H_8O_4$, and *hydrocotoin,* $C_{15}H_{14}O_4$.

Daphnin, $C_{15}H_{16}O_9$, is the crystalline glucoside of the bark of *Daphne Mezereum* (*Mezerei Cortex,* B.P.). Boiled with dilute acids, it yields *daphnetin,* $C_9H_6O_4$, and glucose. The acrid principle of mezereon is resinoid.

Digitalin, $C_5H_8O_2$, Schmiedeberg; $C_{35}H_{56}O_{14}$, Kiliani. —This is an active principle of the Foxglove, *Digitalis purpurea.* Three different glucosides have been prepared from the leaves and seeds of digitalis:—*digitalin, digitonin,* and *digitoxin* (digitoxin occurring in the leaves only). The preparation known as commercial digitalin has been shown to consist of mixtures containing more than one of these glucosides.

The process for the preparation of commercial digitalin consists in extracting digitalis-leaves (*Digitalis Folia,* B.P.) with alcohol (90 per cent.), distilling off the alcohol, dissolving the residue in water containing a small quantity of acetic acid, removing much of the colour from the solution by means of animal charcoal, neutralizing most of the acetic acid with ammonia, precipitating the glucosides by adding tannic acid (with which they form insoluble compounds), washing the precipitate, rubbing and heating it with alcohol (90 per cent.) and lead oxide (which removes the acid as insoluble lead tannate), again decolorizing by means of animal charcoal, evaporating to dryness, washing out with ether any impurities still remaining, and drying the residue. The product is uncrystallizable and somewhat indefinite.

Pure digitalin is prepared from commercial digitalin by dissolving the latter in 4 times its weight of 95 per cent. alcohol, adding 5 times its weight of ether, separating the liquid from undissolved matter and evaporating it in vacuo to about two-thirds of its volume, adding water, filtering off and washing the precipitated crude digitalin, and then recrystallizing this from 95 per cent. alcohol. The pure product is colourless and granular, but it can also be obtained in needle-shaped crystals. It is sparingly soluble in water, ether, and chloroform, but easily soluble in alcohol. When moistened with sulphuric acid and exposed to the vapour of bromine, a violet colour is produced. On hydrolysis digitalin yields *digitaligenin*, $C_{22}H_{30}O_3$; *digitalose*, $C_7H_{14}O_5$, and glucose.

Digitonin, $C_{27}H_{46}O_{14}$.—This glucoside, which does not possess the physiological action characteristic of digitalis, is closely allied to saponin. It yields on hydrolysis *digitogenin*, $C_{15}H_{24}O_3$, galactose, and glucose.

"*Digitaline crystallisée.*"—On treating commercial digitalin with chloroform an inert substance remains undissolved. The solution yields on evaporation a substance known in France as *digitaline crystallisée* which is apparently identical with digitoxin; it may be crystallized from alcohol (90 per cent.) in radiating needles (Nativelle). The therapeutic effect of this substance is identical with that of the preparations of digitalis, but more constant in its action, and, of course, intensely powerful.

Digitoxin, $C_{34}H_{54}O_{11}$, is the highly poisonous glucoside of digitalis leaves. It yields on hydrolysis *digitoxigenin*, $C_{22}H_{32}O_4$, and *digitoxose*, $C_6H_{12}O_4$.

Elaterin, $C_{20}H_{28}O_5$.—Boil elaterium (*Elaterium*, B.P.), the dried sediment from the juice of the squirting-cucumber fruit, with chloroform, filter, evaporate, wash the precipitated elaterin with ether, recrystallize it from chloroform and again wash the crystals with ether. The product, *Elaterinum*, B.P., occurs in small hexagonal plates or prisms.

Elaterin is probably not a true glucoside. It does not always respond to the test for glucose after boiling with acids; and when it does, the reaction is possibly due to *prophetin*, a glucoside stated by Walz to be present in elaterium.

Elaterin is the active principle of the so-called elaterium. Elaterium occurs in light friable greenish-grey cakes. Good specimens of this drug should yield not less than 20 per cent. of elaterin by the above process.

Test.—Elaterin is placed in a watch-glass with a drop of liquefied carbonic acid, and then two drops of concentrated sulphuric acid: a carmine colour is developed (Lindo).

Frangulin, $C_{21}H_{20}O_9$, is a glucoside found in the bark of *Rhamnus frangula.* On hydrolysis it yields *emodin,* $C_{15}H_{10}O_5$, and an unfermentable sugar, *rhamnose,* $C_6H_{12}O_5$.

Gentiopicrin, or Gentian-bitter, $C_{20}H_{30}O_{12}$, the neutral crystalline principle of the root of *Gentiana lutea* (*Gentianæ Radix,* B.P.). It is soluble in water and dilute alcohol. Alkalies decompose it. Dilute acids convert it into *gentiogenin* and glucose. Gentian root also contains a variety of tannin and a crystalline acid, $HC_{14}H_9O_5$, termed *gentianic,* or *gentisic acid,* or *gentisin.* Fused caustic potash, etc., give with the latter an acid ($C_7H_6O_4$), which has also, unfortunately, been called gentisic acid.

Glycyrrhizin or *Glycyrrhizic Acid,* $C_{24}H_{36}O_9$, Gorup-Besanez; $C_{44}H_{63}NO_{18}$, Habermann.—Liquorice-root (*Glycyrrhizæ Radix,* B.P.), in addition to uncrystallizable sugar contains 3 or 4 per cent. of a sweet substance, *glycyrrhizin,* which, when boiled with hydrochloric acid or dilute sulphuric acid, yields a resinoid bitter substance, *glycyrretin,* and an uncrystallizable sugar resembling glucose. Glycyrrhizin is present in *Extractum Glycyrrhizæ,* B.P., *Extractum Glycyrrhizæ Liquidum,* B.P., and in the evaporated decoction (*Stick Liquorice, Spanish Liquorice,* or *Solazzi Juice*). It is soluble in ammoniacal water. The tropical substitute for liquorice is the root of *Abrus precatorius,* or *Indian Liquorice* (*Abri Radix,* P.I.), the *kunch* or *gunj* of Bengal, the *ratti* of Hindustan, and the *jequirity* or *jequerity* of Brazil, which also contains glucose and glycyrrhizin. The seeds yield by maceration a substance which acts as a poison when injected into the blood, but not when swallowed. Warden and Waddell regard the active principle as an albumenoid and term it *abrin.* Bruylants and Venneman consider it to be a product of germination, and call it *jequeritin.* Bechamp and Dujardin regard the latter as a mixture of legumin and *jequerityzymase.* Glycyrrhizin has considerable power of disguising nauseous flavours. Roussin refers the sweet taste of liquorice not to pure glycyrrhizin but to a combination of glycyrrhizin with alkalies, and states that ammoniacal glycyrrhizin has exactly the sweetness of liquorice-root. The formula of this *ammonium glycyrrhizate* is said by Habermann to be $(NH_4)_3C_{44}H_{60}NO_{18}$. Sestini finds that the glycyrrhizin of liquorice-root is chiefly calcium glycyrrhizate.

Guaiacin.—Resin of guaiacum (*Guaiaci Resina*, B.P.), an exudation from the wood (*Guaiaci Lignum*, B.P.) of *Guaiacum officinale*, is probably a mixture of several substances, among which are *guaiaretic*, or *guaiaretinic acid*, $C_{20}H_{26}O_4$ (Hlasiwetz), *guaiaconic acid*, $C_{20}H_{24}O_5$, and *guaiacin*, a glucoside. A lozenge and a tincture of guaiacum are official (*Trochiscus Guaiaci Resinæ*, B.P., and *Tinctura Guaiaci Ammoniata*, B.P.). On boiling guaiacum resin with dilute sulphuric acid for some time, glucose is found in the liquid, a green resinous substance (*guaiaretin*) remaining insoluble (Kosmann). Most oxidizing agents, and even atmospheric air, especially under the influence of certain organic substances, produce a blue, then green, and finally a brown colour when brought into contact with an alcoholic solution of guaiacum resin. Ferric chloride is the official test for this purpose. These effects are said to be due to three stages of oxidation (Jonas). They may be observed on adding the solution to the inner surface of a paring of a raw potato.

Helleborin, $C_{36}H_{42}O_6$, and Helleborein, $C_{26}H_{44}O_{15}$, are crystalline glucosides occurring in the roots of Black Hellebore (*Helleborus niger*), or Christmas rose, and Green Hellebore (*H. viridis*), ranunculaceous herbs. The former is insoluble in water, but soluble in ether; the latter soluble in water, but insoluble in ether.

Jalapin, $C_{54}H_{96}O_{27}$, and Convolvulin, $C_{34}H_{56}O_{16}$.—Some confusion exists regarding the names of these substances, the British and the Continental usages being different. The glucoside jalapin is now almost uniformly called convolvulin in Germany, while the German jalapin, which appears to be identical with scammonin, is generally called convolvulin in Britain. Jalap-resin contains these two distinct substances —convolvulin, chiefly obtained from Mexican male jalap (*Ipomœa Orizabensis*), and jalapin, most largely contained in the true jalap (*Ipomœa purga*); the former is soluble in ether, the latter insoluble. Flückiger advocated the names *jalapurgin* for the ether-insoluble jalapin and *orizabin* for convolvulin, soluble in ether, but these names have not been generally adopted.

Jalap-resin (*Jalapæ Resina,* B.P.) is obtained by digesting and percolating jalap tubercles (*Jalapa,* B.P.) with alcohol (90 per cent.), adding a little water, distilling off the alcohol, pouring away the aqueous portion, which contains much saccharine matter, and washing and drying the residual resin. Jalap thoroughly exhausted by this process should furnish, according to the British Pharmacopœia, not less than 9 nor more than 11 per cent. of resin, of which resin (*Jalapæ Resina,* B.P.) not more than one-tenth should be soluble in ether, a test which excludes resin of Tampico jalap and scammony resin, both of which are soluble in ether. The tincture of jalap is sometimes decolorized by animal charcoal, and the evaporated product sold as "jalapin."

Jalap-resin is insoluble in oil of turpentine; common resin or rosin, soluble. If the presence of the latter is suspected, the specimen should be powdered, digested in turpentine, the mixture filtered, and the filtrate evaporated; no residue, or not more than that yielded by the turpentine itself, should be obtained.

Tampico Jalap, from *Ipomœa simulans,* yields a resin which apparently is chiefly convolvulin, but sometimes contains jalapin; for a sample obtained by Hanbury was entirely soluble in ether, and another extracted by Umney was almost wholly soluble, while Evans purified some, of which only half was soluble.

The *Kaladana resin* (*Kaladanæ Resina,* B.P. Add. 1900, Syn. *Pharbitisin*) obtained from the dried seeds of *Ipomœa hederacea,* Syn. *Pharbitis Nil* (also in the old P.I.) is a resin analogous to, if not identical with, resin of jalap.

Turpethum, Turpeth (B.P. Add. 1900) is the dried root and stem of *Ipomœa Turpethum.* It contains *turpethin,* a resinoid glucoside resembling jalapin in properties. The word *turpeth* is in Persian *turbid,* a cathartic, or *turbad* a cathartic root.

LOGANIN, $C_{25}H_{34}O_{14}$, is a glucoside obtained from the pulp of the fruit and from the seeds of *Strychnos Nux-vomica,* Loganiaceæ (*Nux Vomica,* B.P.), by Dunstan and Short.

Boiled with dilute sulphuric acid, it yields glucose and *loganetin.*

Ouabaïn, $C_{30}H_{46}O_{12}$ (Arnaud); or $C_{30}H_{52}O_{14}$, is a very poisonous glucoside resembling strophanthin, found in the wood of an *acokanthera* and in arrow poisons prepared from this wood.

Picrorhizin is a bitter crystalline glucoside existing, to the extent of 15 per cent., in the dried rhizome of *Picrorhiza Kurroa* (*Picrorhiza,* B.P. Add. 1900). Boiled with 1 per cent. aqueous hydrochloric acid, it yields glucose and resinoid *picrorhizetin.* Picrorhiza is said also to contain cathartic acid (Hooper).

Picrotoxin (*Picrotoxinum,* B.P.) is a crystalline bitter poisonous principle (*πικρὸς, picros,* bitter, and *τοξικὸν, toxicon,* poison) occurring in *Cocculus Indicus,* the dried fruits of *Anamirta paniculata.* Ludwig regarded it as a glucoside; but its constitution is not yet satisfactorily ascertained. Barth and Kretschy state that the so-called picrotoxin may be separated into *picrotoxin* proper, $C_{15}H_{16}O_6$, H_2O, which is bitter and poisonous; *picrotin,* $C_{25}H_{30}O_{12} + nH_2O$, which is bitter but not poisonous; and *anamirtin,* $C_{19}H_{24}O_{10}$, which is neither bitter nor poisonous. Schmidt asserts that the original picrotoxin is definite, and has the formula $C_{30}H_{34}O_{13}$, but that some solvents decompose it into *picrotoxinin,* $C_{15}H_{16}O_6$, which is poisonous, and *picrotin,* $C_{15}H_{18}O_7$, which is not poisonous.

Polychroite, *see* p. 644.

Quassin, $C_{10}H_{12}O_3$, Wiggers; or $C_{31}H_{42}O_9$, Christensen, obtained from *Quassiæ Lignum,* B.P., is said to be a glucoside; but Oliveri and Denaro question the statement, and find quassin to have the formula $C_{32}H_{44}O_{10}$.

Salicin, $C_{13}H_{18}O_7$.—This substance (*Salicinum,* B.P.) is contained in and easily extracted from the bark of various species of willow (*Salix*) and of *Populus.* It occurs in white, shining, bitter crystals, soluble in 28 parts of water or 60 of alcohol (90 per cent.) at ordinary temperatures.

Tests.—1. To a small portion of salicin placed on a white plate or dish, add a drop of concentrated sulphuric acid; a deep red colour is produced.

2. Boil salicin with dilute sulphuric acid for some time; it is converted into *saligenin* or *saligenol,* $C_7H_8O_2$, and glucose. Test for the latter by the copper test.

$$\underset{\text{Salicin}}{C_{13}H_{18}O_7} + \underset{\text{Water}}{H_2O} = \underset{\text{Saligenol}}{C_6H_4(OH)CH_2OH} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

3. To another portion of the liquid, carefully neutralized, add a ferric salt: a purplish-blue colour is sometimes produced, due to the reaction of the saligenin and the ferric salt. The saligenin is, however, so rapidly decomposed by acids into *saliretin,* C_7H_6O, and water, that this reaction is almost valueless as a test. The saligenin may, however, be obtained by the action of synaptase on salicin.

4. Heat a mixture of about 1 part of salicin, 1 of potassium bichromate, 1½ of sulphuric acid, and 20 of water in a test-tube; a fragrant characteristic odour is evolved, due to the formation of salicylaldehyde, $C_6H_4OH{\cdot}COH$, an essential oil identical with that existing in meadow-sweet (*Spiræa Ulmaria*) and in heliotrope.

$$\underset{\text{Saligenol}}{C_6H_4OH{\cdot}CH_2OH} + \underset{\substack{\text{Nascent}\\\text{oxygen}}}{O} = \underset{\text{Salicylaldehyde}}{C_6H_4{\cdot}OH{\cdot}COH} + \underset{\text{Water}}{H_2O}$$

Santonin, $C_{15}H_{18}O_3$.—This substance is, apparently, the anhydride or, rather, lactone,* of a weak acid (Hesse) insoluble in ammonia, but forming a soluble calcium salt. Indeed, by boiling santonin for twelve hours with baryta water, Cannizzaro has obtained a salt from which hydrochloric acid separates *santonic acid,* $C_{15}H_{20}O_4$. From a solution of calcium santonate the santonin is precipitated by acids. Boiled for some time with dilute sulphuric acid, it yields 87 per cent. of an insoluble resinous substance (*santoniretin*) and glucose (Kosmann). Santonin (*Santoninum,* B.P.) is official; it is soluble in an aqueous solution of twice its weight of sodium carbonate. Possibly (Berthelot) santonin resembles carbolic acid,—in other words, is a phenol, $C_{15}H_{15}(OH)_3$. Its glucosidal character is questionable.

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* Certain hydroxyacids, by loss of water, yield *lactones.* Aromatic compounds containing NH_2 in the ortho position and losing water by the oxidation and removal of one or two atoms of that hydrogen furnish bodies which may be distinguished as *lactams* and *lactims.*

Process.—The process for its preparation consists in boiling santonica (the dried unexpanded flower-heads or capitula of *Artemisia maritima*) with milk of lime (whereby calcium santonate is formed), straining, precipitating the santonin or santonic acid by the addition of hydrochloric acid, washing with ammonia to remove resin, dissolving in alcohol and digesting with animal charcoal to get rid of colouring-matter, setting the alcoholic solution aside to deposit crystals of santonin, and purifying by recrystallization from alcohol (Mialhe).

Test.—To highly diluted solution of ferric chloride add an equal volume of concentrated sulphuric acid. To this reagent add the santonin or powder or substance suspected to be santonin, and cautiously apply heat. A red, purple, and finally violet colour is produced (Lindo). Santonin added to warm alcoholic solution of caustic potash yields a violet-red colour.

SAPONIN, $C_{32}H_{52}O_{17}$, H_2O, is a peculiar glucoside occurring in Soapwort, *Saponaria*, the root of the common Pink, and many other plants; its solution in water, even though very dilute, froths like a solution of soap. Heated with dilute acid it yields glucose and *sapogenin*, $C_{14}H_{22}O_2$. Pereira considered *smilacin* (*salseparin* or *parallin*), one of the principles of the supposed activity of Sarsaparilla (*Sarzæ Radix*, B.P.), to be closely allied to, if not identical with, saponin. According to Klunge ("Pharmacographia"), parallin, by action of acids, yields *parigenin*. The aqueous solutions of parallin froth when shaken. Von Schultz states that sarsaparilla contains three homologous glucosides analogous to saponin, namely, sarsaparill-saponin, $C_{20}H_{32}O_{10}$, sarsa-saponin, $C_{22}H_{36}O_{10}$, and parallin, $C_{26}H_{44}O_{10}$.

Saponin is also met with in the root of *Polygala Senega* (*Senegæ Radix*, B.P.), though the activity of senega is said to be due to two glucosides, *senegin* and *polygalic acid*.

Saponin is readily obtained from the bark of *Quillaja saponaria*, or *soap-bark* (*Quillaiæ Cortex*, B.P.), by boiling the aqueous extract in alcohol and filtering while hot. Flocks of saponin separate on cooling. It is a white, non-crystalline, friable powder.

The alleged toxic properties of commercial saponin are said by Kobert to be due to *sapotoxin* and *quillaic acid* which seem to be identical with senegin and polygalic acid respectively.

Scammonin, $C_{34}H_{56}O_{16}$ (apparently identical with the substance called convolvulin in Britain).—Boil resin of scammony (*Scammoniæ Resina*, B.P.) with dilute sulphuric acid for some time; glucose may then be detected in the liquid, a resinous acid termed *scammonolic acid*, $C_{16}H_{30}O_3$, being produced at the same time. This acid is also obtained by the hydrolysis of convolvulin. According to Kromer, scammonin is oxidized by nitric acid into oxalic, valeric, and butyric acids, carbonic anhydride, and an acid melting at 101° C., which is isomeric with sebacic acid. Potassium permanganate oxidizes scammonin to oxalic and valeric acids, and the monobasic scammonolic acid. Kromer gives the formula for scammonin as $C_{88}H_{156}O_{42}$.

Natural scammony (*Scammonium*, B.P.) is an exudation from incisions in the living root of *Convolvulus Scammonia*. It contains from 10 to 20 per cent. of gum, and, therefore, when triturated with water, gives an emulsion. "It should yield at least 70 per cent. of resin soluble in ether." The official resin of scammony contains no gum, and therefore gives no emulsion when triturated with water. It is prepared by digesting the dried root (*Scammoniæ Radix*, B.P.) in alcohol (90 per cent.), distilling off the greater part of the alcohol, pouring the remaining liquid into water and washing the precipitated resin with boiling water till free from gum. There seems to be little or no chemical difference between the extracted resin and the resin of the exuded scammony.

Scammony Resin is almost entirely soluble in ether. Spirgatis states that it is identical with the resin of Mexican Male Jalap, which also is soluble in ether. Sulphuric acid slowly reddens it. It is said to be liable to adulteration with resin of true jalap, guaiacum-resin, and common rosin. Resin of true jalap is insoluble in ether, guaiacum-resin is distinguished by the colour-tests mentioned under Guaiacin, and rosin is recognised by the action of sulphuric acid.

Scillain.—Schroff, and, afterwards Riche and Remont, believed the bitter principle of the squill-bulb (*Scilla*, B.P.) to be a glucoside. Merck has extracted substances which he has termed *scillipicrin*, *scillitoxin*, and *scillin*, and to which the bitter taste of squill is due. Scillitoxin appears to be identical with the scillaïn of v. Jarmerstedt. Schmiedeberg has given the name *sinistrin* to a squill carbohydrate. Squill contains a large quantity of mucilage.

The bulbous root of *Crinum Asiaticum* is included in the Pharmacopœia of India (*Crini Radix*, P.I.), as a substitute for squill. It has not been chemically investigated.

STROPHANTHIN, $C_{32}H_{48}O_{16}$, Feist; $C_{31}H_{48}O_{12}$, Arnaud.—According to Fraser, this is the active principle of strophanthus seeds (*Strophanthi Semina*, B.P.) the dried seeds of *Strophanthus Kombé*, and is a glucoside. He obtained it in crystals. Acids convert it into glucose and crystalline *strophanthidin*. Phosphomolybdic acid produces in solutions of strophanthin a bright bluish-green colour. Feist states that it yields very little, if any, glucose on hydrolysis, but gives, in addition to strophanthidin, a white crystalline substance of the formula $C_{13}H_{24}O_{10}$, melting at 207° C., and a sugar of unknown composition. Kohn and Kulisch have also investigated strophanthin, but they are inclined to accept Arnaud's formula, and to doubt the correctness of Fraser's view of the glucosidal nature of strophanthin. Helbing states that its aqueous solution yields, with a trace of solution of ferric chloride and some concentrated sulphuric acid, a reddish-brown precipitate which after an hour or two turns green. Sulphuric acid colours strophanthin dark green, changing to reddish brown. Possibly strophanthin is only one of the active principles of the different species of strophanthus. Strophanthus seeds are used in the preparation of *Tinctura Strophanthi*, B.P. They contain nearly one-third of their weight of oil.

QUESTIONS AND EXERCISES

Define glucosides, and mention those of pharmaceutical interest.—Construct an equation illustrative of the formation of oil of bitter almonds from amygdalin.—How much pure amygdalin will yield one grain of hydrocyanic acid?—To what does cherry-laurel water owe its activity?—Mention the active principle of senna.—State the circumstances under which guaiacum-resin yields glucose.—Mention a test for guiacum-resin.—How may the adulteration of jalap-resin by rosin be detected?—Enumerate the tests for salicin.—How is santonin officially prepared?—Name sources of saponin.—What is the difference between scammony and resin of scammony?—How would you detect resins of turpentine, guaiacum, or jalap, in resin of scammony?

UNCLASSIFIED MEDICINAL PRINCIPLES, ETC.

The following articles, employed medicinally in such forms as Decoction, Extract, Infusion, Tincture, etc., contain active principles which have not yet been thoroughly examined. Some of these principles have been isolated, and a few have been obtained in the crystalline condition; but their constitution has not been sufficiently well made out to admit of the classification of the bodies either among alkaloids, glucosides, acids, or other well-marked principles.

Agropyrum, B.P. Add. 1900, or *Triticum*, U.S.P., Couch-grass.

Andrographis (B.P. Add. 1900), *Andrographis Caules et Radix*, P.I., from *Andrographis paniculata*, Kariyat, a bitter principle.

Anthemidis flores.

Apocynum. Canadian hemp.

Asclepias Tuberosa. Pleurisy root. (Asclepedin.)

Aurantii cortex. (Hesperidin.)

Azadirachta Indica, Indian Azadirach (B.P. Add. 1900); *Azadirachtæ Cortex et Folia*, P.I., from *Melia azadirachta*, Neem or Margosa. (A resin; $C_{36}H_{50}O_{11}$. Broughton.)

Bonducellæ Semina, P.I., from *Cæsalpinia* (*Guilandina*) *Bonducella. Bonduc-seeds or nickar-nuts.*

Buchu folia.

Buteæ Semina, B.P. Add. 1900.

Calendula officinalis. Marigold (Calendulin, Stoltze.)

Calotropis, B.P. Add. 1900, and P.I., from *Calotropis procera* and *C. gigantea.* Mudar.

Canellæ cortex. (Cascarillin, $C_{12}H_{11}O_4$.)

Caulophyllum Thalictroides. Blue cohosh. Alkaloid?

Cimicifuga (*Actæa*) *racemosa* (Cimicifugin; said by Conard to be neutral, and by Falck alkaloidal). Black snake-root. (*Cimicifugæ Rhizoma*, B.P.)

Cucurbitæ Semina Præparata, melon pumpkin seeds, B.P. Add. 1900, or *Pepo*, from *Cucurbita maxima*, *Duch.* (*Cucurbita Pepo*, Linn.). A remedy for tape-worm.

Cypripedium pubescens (Cypripedin?). Ladies' slipper.

Euonymus atropurpureus. Wahoo-bark. (Euonymin?)

Euonymi Cortex, B.P., is "the dried root bark," the source of *Extractum Euonymi Siccum*, B.P.

Eupatorium perfoliatum. Thoroughwort or Boneset.

Gossypii Radicis Cortex. Cotton Root Bark, B.P. Add. 1900.

Gulancha tinospora, B.P. Add. 1900, the dried stem of *Tinospora cordifolia* (*Tinosporæ Radix et Caules*, P.I.).

Hamamelis Virginica. Witch-hazel.

The official portions are *Hamamelidis Cortex*, B.P., the source of *Tinctura Hamamelidis*, B.P., and *Hamamelidis Folia*, B.P., the source of *Extractum Hamamelidis Liquidum*, B.P.

Hydrocotyles Folia, P.I., from *Hydrocotyle Asiatica.* Indian pennywort.

Hygrophila (B.P. Add. 1900), the dried herb, *Hygrophila spinosa.*

Iris versicolor. Blue flag. (Iridin or Irisin?)

Kara (*Karæ Rhizoma*, B.P. Add. 1900), a remedy in alcoholism.

Lactuca. (Lactucin, etc.) The milk-juice, dried, yields *Lactucarium*, U.S.P.

Lappa, U.S.P., *Arctium Lappa*, *Lappa officinalis.* Burdock.

Lupulus.

Magnolia. Swamp sassafras, or beaver tree.

Marrubium. Horehound. Marrubein, a crystalline bitter substance (Mein).

Maticæ Folia. Matico.

Phytolacca Bacca et Radix. Poke-berry and root. Phytolaccin, a crystalline substance (Claassen).

Scutellaria. Skullcap.

Soymidæ Cortex, P.I., Rohun Bark, from *Soymida febrifuga.*

Taraxaci Radix. (Taraxacin.)

Toddalia, the dried root-bark of *Toddalia aculeata*, B.P. Add. 1900; *Toddaliæ Radix*, P.I.

Triticum repens. Rhizome of couch-grass. See *Agropyrum*, *ante.*

Veronica Virginica, roots and rhizome. Culvers root; *Leptandra*, U.S.P. (Leptandrin ?).

Viburnum. Black haw, B.P. Add. 1900; and U.S.P. (*Viburnin*).

ALKALOIDS

Constitution of Alkaloids, or Organic Bases.

Natural Alkaloids.—The natural organic bases, alkaloids, or alkali-like bodies (εἶδος, *eidos*, likeness), have certain analogies with ammonia. The constitution of some of them is comparatively simple, while in many cases it is exceedingly complex and has not as yet been fully elucidated. All contain nitrogen, and may be regarded as ammonia which has had its hydrogen replaced wholly or in part by one or more organic groups of greater or less complexity. Some of the more important alkaloids are closely related to pyridine, quinoline, etc., compounds which are referred to further on.

Numerous *artificial organic bases*, having a very simple relation to ammonia, have already been formed. These are commonly called *amines*, and they are primary, secondary, or tertiary according as one, two, or three atoms of hydrogen in ammonia have been replaced by radicals, as seen in the following general formulæ (R = any univalent radical):—

$$\left.\begin{matrix}R\\H\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}R\\R\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}R\\R\\R\end{matrix}\right\}N;$$

or in the following examples:—

$$\underset{\text{Ethylamine}}{\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N} \qquad \underset{\text{Diethylamine}}{\left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}N} \qquad \underset{\text{Triethylamine}}{\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}N}$$

The primary and secondary amines are sometimes called amino-bases and imino-bases respectively.

Formation of some of the Artificial Organic Bases.—A few illustrations will suffice. Just as the addition of hydrogen iodide, HI, to ammonia, NH_3, gives ammonium iodide, NH_4I, so the addition of ethyl iodide, C_2H_5I or EtI (*see* p. 459), to ammonia gives ethyl-ammonium iodide, $NH_3C_2H_5I$ or NH_3EtI. A fixed alkali liberates ammonia from ammonium iodide; it liberates ethyl-ammonia or *ethylamine*, NH_2Et, from ethyl-ammonium iodide. Ethylamine with ethyl iodide, EtI, gives diethyl-ammonium iodide, $NH_2(C_2H_5)_2I$ or NH_2Et_2I. From the latter caustic potash liberates diethyl-ammonia or *diethylamine*, $NHEt_2$. Diethylamine with ethyl iodide gives triethyl-ammonium iodide, $NH(C_2H_5)_3I$ or $NHEt_3I$. The latter with caustic alkali gives triethyl-ammonia or *triethylamine*, NEt_3, and this with ethyl iodide gives tetrethyl-ammonium iodide, $N(C_2H_5)_4I$ or NEt_4I, which is not decomposable by caustic potash.

What has just been stated respecting ethyl iodide is true of a number of other organic iodides, so that a large number of artificial organic bases and their salts can be produced. The reactions are not always so sharp, however, as might be inferred from the preceding paragraph, mixtures of primary, secondary, and tertiary compounds, rather than a single amine, being obtained. Some of these artificial bases not only resemble natural alkaloids, but yield solutions which are strongly caustic liquids, like solution of ammonia.

The radicals in the amines which take the place of the hydrogen in ammonia are not necessarily all of one kind as in the case of the ethyl derivatives referred to above, but two or more different radicals may be present in the same amine. Thus, for example, we have methyl-ethyl-amylamine, $C_8H_{19}N$, or $NCH_3C_2H_5C_5H_{11}$, or NMeEtAy, a colourless, oily substance, of agreeable aromatic odour, while such substances as methyl-ethyl-propyl-isobutyl-ammonium chloride, $NCH_3C_2H_5C_3H_7C_4H_9Cl$, have also been prepared.

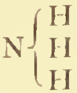
Analogues of Amines.—As might be expected from the analogy of phosphorus, arsenium, and antimony with nitrogen, there are also known *phosphines*, *arsines*, and *stibines*; bases resembling *amines*, but containing the respective elements (P,As,Sb) in place of the nitrogen of the amines.

Methylamine, CH_3NH_2, and *trimethylamine*, $(CH_3)_3N$, have been obtained both artificially and from naturally occurring organic materials. Methylamine was found by Schmidt, in *Mercurialis annua* and *M. perennis,* and previously by Reichardt, who termed it *mercurialine.* Trimethylamine is produced in large quantities in the dry distillation of the evaporated residue of the spent wash produced in beetroot spirit distilleries.

Propylamine, $C_3H_7NH_2$, is a volatile oil, one product of the destructive distillation of bones and other animal matters.

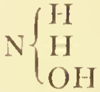
Besides the amines derived from a single molecule of ammonia, which are called *monamines,* there are also *diamines, triamines,* etc., which may be looked upon as derivatives of two, three, etc., molecules of ammonia. Thus ethylene-diamine is represented by the formula $C_2H_4(NH_2)_2$. Diethylene-diamine, $NH(C_2H_4)_2NH$, is used medicinally under the name *piperazine;* its constitution resembles that of piperidine (*see* p. 628), but with the group NH taking the place of a CH_2 group in that compound.

Hydroxylamine.—Besides the various amines already mentioned, ammonia may have one atom of its hydrogen displaced by hydroxyl, hydroxylamine, NH_2OH, resulting. Hydroxylamine is formed by the reduction of the nitric acid, when zinc, dilute sulphuric acid, and a little nitric acid interact. It yields substitution products, as ethylhydroxylamine, NHC_2H_5OH, and addition compounds, as hydroxylamine hydrochloride, NH_2OH,HCl:—



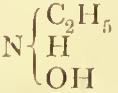
$$N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.$$

Ammonia



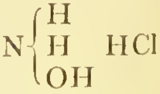
$$N\left\{\begin{matrix}H\\H\\OH\end{matrix}\right.$$

Hydroxylamine



$$N\left\{\begin{matrix}C_2H_5\\H\\OH\end{matrix}\right.$$

Ethyl-hydroxylamine



$$N\left\{\begin{matrix}H\\H\quad HCl\\OH\end{matrix}\right.$$

Hydroxylamine hydrochloride

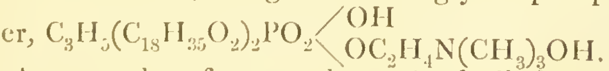
Hydroxylamine and aldehydes yield *aldoximes.* Hydroxylamine and ketones, such as acetone, yield *acetoximes.* (*See* Manuals, not limited to the requirements of medical and pharmaceutical students.)

Hydrazine, $H_2N—NH_2$. Diethylamine, by action of nitrous acid, yields a nitroso-derivative which, on reduction, furnishes what apparently is a diamidic compound—diethylhydrazine, $(C_2H_5)_2N—NH_2$. Hydrous hydrazine has the formula $H_2N—NH_2,H_2O$. Hydrazine itself cannot very easily be isolated. Its salts with ordinary acids are generally crystalline, and isomorphous with corresponding ammonium salts. Acidulated, they have very powerful reducing properties, and act as strong poisons towards the lower organisms. *Phenylhydrazine*, $C_6H_5HN—NH_2$, is an extremely useful agent; employed in making phenazone, various colouring-matters, etc. It forms important compounds with the sugars.

Azoimide or *imidazoic acid*, HN_3, is a substance closely resembling the haloid acids, and was originally prepared by Curtius from hydrazine and ethyl hippurate; it may, however, be prepared more easily by a method proposed by Wislicenus, in which sodamide, $NaNH_2$, prepared by passing ammonia over melted sodium, is heated with nitrous oxide.

Plant Alkaloids.—These are of great importance to the medical and pharmaceutical student. They are treated in considerable detail in the succeeding pages.

Animal Alkaloids.—Many well-known alkaloids occur in the juice of the flesh, and in other parts of animals. Ordinary extract of meat contains abundance of crystals of *creatine*, $C_4H_9N_3O_2$, and some *creatinine*, $C_4H_7N_3O$. Creatine easily parts with the elements of water and yields creatinine; it takes up the elements of water and yields *sarkosine*, $C_3H_7NO_2$, and *urea*, CH_4N_2O. Sarkosine is methyl-glycocoll. *Taurine*, $C_2H_7NSO_3$, may be obtained from bile; and it can be constructed artificially from its elements. Some animal tissues, as of the spleen, brain, and pancreas, yield, as a product of work, *leucine*, $C_6H_{13}NO_2$, which occurs in white, pearly crystals; also *tyrosine*, $C_9H_{11}NO_3$. *Lecithin*, which occurs in yolk of egg and in the brain, is a highly complex choline derivative, being a distearic glycerophosphoric choline ester,



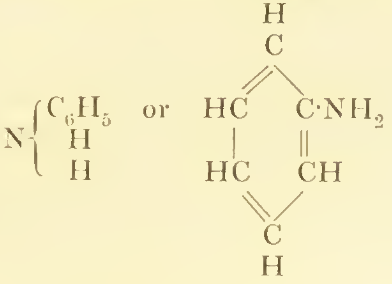
$$C_3H_5(C_{18}H_{35}O_2)_2PO_2\begin{cases}OH\\OC_2H_4N(CH_3)_3OH.\end{cases}$$

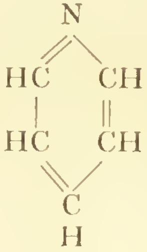
As examples of some other animal alkaloids, Gautier has obtained several new alkaloids from albumenoids, and hence has termed them *leucomaines* (*λεύκωμα*, *leucoma*, white of egg), namely, *xanthocreatinine*, $C_5H_{10}N_4O$, *crusocreatinine*, $C_5H_8N_4O$, *amphicreatinine*, $C_9H_{19}N_7O_4$, and *pseudoxanthine*, $C_4H_5N_5O$. The leucomaines and the animal alkaloids generally are of great physiological interest. Some of the leucomaines are toxic and indistinguishable from ptomaines; in fact, the three classes merge into one another.

Ptomaines.—A series of diamines, many of them toxic, have been isolated, by Brieger, from decaying nitrogenous animal principles, including the putrid albumenoids or proteids of the human body itself—hence the name *ptomaines* (πτῶμα, *ptoma*, a corpse). These have some medico-legal importance, but, inasmuch as they may occur in the living body, poisoning the blood during the progress of disease, especially disease associated with the development of micro-organisms or microbes, that is, zymotic disease (ζύμη, *zumē*, leaven or ferment), they have great pathological interest—indeed, physiological interest also, for one of a curari-like character seems to play a part in the process of digestion. The names of some of these bases are *neurine*, $C_5H_{13}NO$, and *neuridine*, $C_5H_{14}N_2$, from putrid flesh; *muscarine*, $C_5H_{13}NO_2$, and *gadinine*, $C_7H_{16}NO_2$, from putrid fish; *cadaverine*, $C_5H_{16}N_2$, *saprine*, and *putrescine*, $C_4H_{12}N_2$, from putrid human remains, *choline* being met with in the earlier stages of decay; and *tetanine*, $C_{13}H_{30}N_2O_4$, (the administration of which to animals produced symptoms resembling those of tetanus in man), from beef putrefied by the agency of the microbe which is associated with the cause of traumatic tetanus, so distressing to the human subject. *Tyrotoxicon* was the name given by Vaughan to a toxic ptomaine he isolated from poisonous cheese (τυρὸς, *turos*, cheese; τοξικόν, *toxicon*, poison), afterwards from poisonous milk and cream, which, taken as food, had caused more or less vomiting, headache, and diarrhœa. Brieger states that when shell-fish is poisonous this is due to the presence of a ptomaine he has named *mytiloxine*, $C_6H_{15}NO_2$. Para- and meta-phenylene-diamine appear to have all the characters of leucomaines or ptomaines, the latter causing intense influenza.

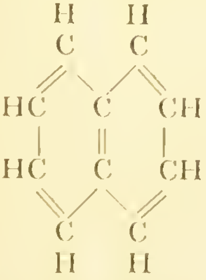
Alkaloids of both Plant and Animal Origin.—*Choline*, $C_5H_{15}NO_2$, occurs in the bile and the brain, also in ergot and ipecacuanha, hops, areca nut, cotton-seed cake, *Scopola Japonica*, etc. *Guanine*, $C_5H_5N_5O$, and *sarkine*, $C_5H_4N_4O$, are found in flesh and in young plant leaves. Fresh meat furnishes *carnine*, $C_7H_8N_4O_3$, which also occurs in yeast; and *betaine*, $C_5H_{11}NO_2$, is found in beetroot, cotton-seed cake, and in urine.

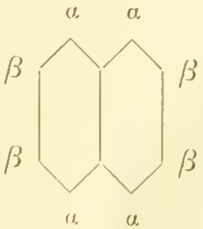
Attempts to form artificially the more important natural organic bases commonly used in medicine have for the most part failed, although a few alkaloids, identical with the natural substances, have been obtained synthetically (*e.g.*, atropine and conine). Many artificial colorific alkaloids of the amidobenzene (aniline or phenylamine) type, and of a curious double nitrogen type (*diazobenzene* $= C_6H_5{\cdot}N : N{\cdot}OH$) have been obtained. But the type of the natural medicinal alkaloids seems to be more closely related to *pyridine,* C_5H_5N, and to *quinoline* or *chinoline,* C_9H_7N. Pyridine is producible in various ways, but is contained in *bone-oil* (from the distillation of bones—whence, also, *pyrrol,* C_4H_5N, and thence *iodopyrrol,* or *iodol,* C_4I_4HN, a rival of iodoform), together with the homologues *picoline,* C_6H_7N (or methyl-pyridine, ortho-, meta-, or para-) ; *lutidine,* C_7H_9N ; *collidine,* $C_8H_{11}N$; etc. ; forming an homologous series of *pyridine bases,* $C_nH_{2n-5}N$.


Phenylamine or amido-benzene

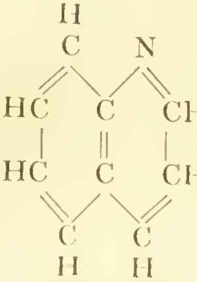

Pyridine

From quinine, cinchonine, and strychnine, by the disruptive action of caustic alkalies, not only pyridine and homologues, but also quinoline have been obtained. Quinoline can be made in various other ways, especially (Skraup) from nitrobenzene, aniline, and glycerin. Quinoline is closely related both to benzene and to pyridine (*see* the following formula). Its relation to naphthalene (two carbon-conjoined benzene residues) is similar to that of pyridine to benzene.


Naphthalene



Alpha and beta positions


Quinoline

Both pyridine and quinoline form additive compounds with hydrogen (*see* Piperidine, p. 628).

By adding six atoms of hydrogen to pyridine, piperidine is obtained; and conine, the alkaloid of hemlock, is piperidine with propyl (C_3H_7) replacing one of the hydrogen atoms. It has been formed artificially by Ladenburg from picoline (*see* also ecgonine, tropine, etc.).

Chemists, in the hope, doubtless, of discovering how to produce the valuable medicinal alkaloids artificially, have prepared a number of alkaloidal derivatives of quinoline. One of them, *kairine*, somewhat resembles quinine.

It seems reasonable to suppose that the study of the constitution of the alkaloids, in light of the products resulting from the various decompositions which they undergo, will in time lead chemists to the successful synthesis of, at least, some of the most important alkaloids. Indeed, the rapid progress of investigation and the consequent extension of our knowledge of this department of chemistry, justify the inference that we are at last almost "within measurable distance" of the artificial production of most of the natural alkaloids. This is a subject of financial and general commercial weight; of considerable technological, including pharmaceutical, importance; of very great medical consequence, especially taken in connection with its ramifications; and of transcendent scientific interest as illustrating the working of nature's forces within the molecules of matter.

Note on Nomenclature of Natural Alkaloids.—The first syllables of the names of the natural alkaloids frequently recall the name of the plant from which they are obtained, or some characteristic property, while the final syllable is either *ine* or *ia*. The compilers of the American, British, French, and German Pharmacopœias have uniformly adopted the termination *ine*. The names of the salts of the alkaloids are given on the assumption that the acid simply unites with the alkaloid without the elimination of water. Thus morphine hydrochloride (sometimes termed "hydrochlorate") is regarded as morphine which has united with hydrochloric acid. Acids in general unite with alkaloids and form additive salts of a similar kind.

Antidotes.—In cases of poisoning by alkaloids, emetics and the stomach-pump must be relied on rather than chemical agents. But astringent liquids may be administered, for tannic acid precipitates many of the alkaloids from their aqueous solution, absorption of the poison possibly being thus retarded.

MORPHINE AND OTHER OPIUM ALKALOIDS

Morphine

Occurrence.—Morphine or morphia, $C_{17}H_{19}NO_3,H_2O$, occurs in opium (the inspissated juice of the seed-capsule of the White Poppy, *Papaver somniferum*) perhaps partly as morphine meconate [$(C_{17}H_{19}NO_3)_2,C_7H_4O_7,5H_2O$; Dott] and sulphate. The dried poppy-capsule of pharmacy (*Papaveris Capsulæ*, B.P.) contains opium principles, but they vary much in nature and proportion: the presence of morphine, narcotine, and meconic acid has been demonstrated; also (by Groves) of codeine and narceine. Ordinary Asia-Minor opium (Turkey, Smyrna, or Constantinople opium) contains, when dried, from 10 to 15 per cent. of morphine. The British Pharmacopœia directs that opium used for officially recognised purposes, other than the manufacture of alkaloids, or of extract of opium of official strength, must contain not less than 9·5, and not more than 10·5 per cent. of morphine, when the opium is quantitatively analysed (*see* p. 794) by the official method.

Morphine Hydrochloride.—The hydrochloride, $C_{17}H_{19}NO_3,HCl,3H_2O$ (*Morphinæ Hydrochloridum*, B.P.), occurs in slender white acicular crystals; it is prepared by simply decomposing an aqueous infusion of opium with calcium chloride, calcium meconate and morphine hydrochloride being produced. (If the infusion, which is always acid, be first nearly neutralized by the cautious addition of small quantities of a very dilute solution of ammonia, the calcium chloride then at once causes precipitation of calcium meconate, which can be filtered off, leaving a coloured solution of morphine hydrochloride. On the large scale the details are somewhat different.) The filtered liquid is evaporated, and the impure morphine hydrochloride which crystallizes out on cooling is redissolved in water and treated with animal charcoal; the morphine is then precipitated from the still coloured liquid by addition of excess of ammonia, separated by filtration, and dissolved in hot dilute hydrochloric acid; morphine hydrochloride separates out on cooling.

Morphine hydrochloride deposited from a hot solution in about twenty times its weight of alcohol is anhydrous.

Morphine Acetate and Tartrate.—Morphine acetate,

$C_{17}H_{19}NO_3$, $C_2H_4O_2$, $3H_2O$ (*Morphinæ Acetas*, B.P.), is prepared by dissolving morphine in acetic acid. Morphine tartrate, $(C_{17}H_{19}NO_3)_2$, $C_4H_6O_6$, $3H_2O$ (*Morphinæ Tartras*, B.P.), may be prepared by neutralizing a mixture of morphine and water with tartaric acid. One grain of tartrate in 22 minims of water forms *Injectio Morphinæ Hypodermica*, B.P.

Morphine hydrochloride, acetate, and tartrate are soluble in water, but the solutions are not stable unless acidulated and containing alcohol (*Liquor Morphinæ Hydrochloridi*, B.P., *Liquor Morphinæ Acetatis*, B.P., and *Liquor Morphinæ Tartratis*, B.P.); in preparing the official 1 per cent. solutions, a few minims per ounce of hydrochloric or acetic acid are added in the case of the two former. Even solid morphine acetate is unstable, slowly decomposing into acetic acid and morphine; hence the acid odour of morphine acetate; hence, too, the necessity, when a solution of morphine acetate of perfectly definite concentration is required, of preparing it from a weighed quantity of hydrochloride, or of pure crystalline morphine. Other preparations official in the British Pharmacopœia, are *Suppositoria Morphinæ*, *Trochiscus Morphinæ*, *Trochiscus Morphinæ et Ipecacuanhæ*.

Morphine Sulphate, $(C_{17}H_{19}NO_3)_2$, H_2SO_4,$5H_2O$ is prepared by neutralizing precipitated morphine with dilute sulphuric acid. It occurs in white silky crystals, soluble in water.

Solubility of morphine salts in water at 60° F.—According to Dott, 1 part of the respective salts is soluble in the annexed numbers of parts of water:—acetate, $2\frac{1}{2}$; tartrate, $9\frac{3}{4}$; sulphate, 23; hydrochloride, 24; meconate, 34.

Analytical Reactions.

1. To a minute fragment of a morphine salt add one drop of water and warm the mixture until the salt dissolves, then stir the liquid with a glass rod moistened with concentrated *neutral* solution of ferric chloride; a dirty-blue colour is produced.

Even in dilute solutions morphine reduces potassium ferricyanide to ferrocyanide, hence may be detected by the blue precipitate (Prussian blue) produced on the addition of ferric chloride and ferricyanide. Other substances, but no other official alkaloids, give this reaction.

2. To a drop or two of a concentrated solution of a morphine salt in a test-tube add a minute fragment of iodic acid (HIO_3, p. 317); iodine is set free. Into the upper part of the tube introduce a glass rod moistened with mucilage of starch, and warm the solution; dark-blue "iodide of starch" is produced. If the mixture of morphine and iodic acid be shaken up with chloroform or carbon bisulphide, a violet solution is obtained. This reaction is only confirmatory of others, as albuminous matters also reduce iodic acid.

3. To a few drops of an aqueous infusion of opium add a drop of *neutral* solution of ferric chloride; a red solution of ferric meconate is produced. Add solution of corrosive sublimate; the colour is not destroyed (as it is in the case of ferric thiocyanate, a salt of similar tint). In cases of poisoning by a preparation of opium, this test is almost as conclusive as a direct reaction of morphine (the poison itself), meconic acid being obtainable from opium only.

4. According to Lamal, morphine solutions give, on addition of uranium acetate, a reddish-brown colour, which disappears on adding acids, whilst, on adding caustic alkalies a deep red precipitate is formed, which turns yellow on adding an excess of the reagent. The test is best made by putting 2 to 10 drops of the morphine solution into a porcelain dish and adding the same quantity of uranium solution (0·015 gramme of uranium acetate and 0·01 gramme of sodium acetate in 5 c.c. of water). After evaporating on the water-bath, concentric, bright red or hyacinth-red spots are left. The reaction is still visible with 0·05 milligramme of the alkaloid. Most of the other alkaloids give no reaction; salicylic acid gives brick-red spots; tannin, gallic acid, and pyrogallol brown spots. Phenol gives a brown colour, slowly disappearing on warming. The coloration with uranium acetate is very permanent.

Other Reactions.—Add sodium carbonate to a solution of a morphine salt; a white precipitate of morphine is produced slowly, and is of a crystalline character if the solution is dilute. Collect this precipitate and moisten it with neutral solution of ferric chloride; the bluish tint above referred to is produced.——Add an alkali to a solution of morphine hydrochloride, acetate, or tartrate; morphine is precipitated, soluble in excess of fixed alkali, far less readily so in ammonia.——Moisten a particle of a morphine salt with nitric acid; an orange-red coloration is produced. Warm some morphine with concentrated sulphuric acid and sodium arsenate; a blue-green tinge results.——To morphine add concentrated sulphuric acid, mix, and add powdered bismuth nitrate to the fluid; the mixture turns dark brown or black.——Heat morphine on platinum foil; it burns away entirely.

Codeine

Codeine, or Codeia, $C_{18}H_{21}NO_3$, H_2O, methyl-morphine, is another officially recognised opium alkaloid (*Codeina*, B.P.). It dissolves in the slight excess of ammonia employed for precipitating morphine in the foregoing process for the preparation of morphine hydrochloride. It is obtained by evaporating the ammoniacal filtrate, treating the residue with water, precipitating with caustic potash, and purifying the precipitated alkaloid by recrystallization from ether. Codeine may also be obtained by heating a sodium compound of morphine, $C_{17}H_{18}NaNO_3$, with methyl iodide, CH_3I; sodium iodide and methyl-morphine or codeine result. It occurs "in colourless or nearly colourless trimetric crystals, soluble in 80 parts of water or of solution of ammonia, readily soluble in alcohol (90 per cent.), in chloroform, and in diluted acids. It is soluble in 30 parts of ether. The aqueous solution has a bitter taste and an alkaline reaction. The alkaloid dissolves in an excess of sulphuric acid, forming a colourless solution, a small quantity of which, when gently warmed on a water-bath with 2 drops of solution of ammonium molybdate, or with a trace of ferric chloride or potassium ferricyanide, develops a blue or bluish-black colour, which, on the addition of a minute trace of dilute nitric acid, changes to a bright scarlet, becoming orange. Heated to redness in air, it yields no ash." It reduces a solution of one part of ammonium selenite in twenty of concentrated sulphuric acid, yielding a green colour (Lafon). Codeine neither gives a blue colour with ferric chloride nor a red with nitric acid. Both codeine and morphine when heated with a mixture of concentrated sulphuric acid and sodium arsenate give a blue colour, the morphine yielding a greenish blue and the codeine a violet blue.

Codeine Phosphate is official (*Codeinæ Phosphas,* B.P.), and a syrup is prepared from it (*Syrupus Codeinæ,* B.P.).

Dionin, is ethylmorphine hydrochloride; $C_{19}H_{23}NO_3$, $HCl.H_2O$.

Heroin is diacetylmorphine, $C_{17}H_{17}NO(C_2H_3O_2)_2$. Both the base itself and its hydrochloride are used in medicine.

APOMORPHINE, $C_{17}H_{17}NO_2$

The alkaloid apomorphine (ἀπὸ, *apo,* from, and *morphine*) was obtained from morphine by Matthiessen and Wright. It produces remarkable physiological effects; one-tenth of a grain (in aqueous solution) injected under the skin, or a quarter of a grain taken into the stomach, produces vomiting in from four to ten minutes.

Preparation.—Morphine hydrochloride or codeine hydrochloride is hermetically sealed in a thick tube with considerable excess of hydrochloric acid, and heated to nearly 300° F. (148·8° C.) for two or three hours. The product is purified by diluting the contents of the tube with water, precipitating with sodium bicarbonate, and treating the precipitate with ether or chloroform. On shaking up the ethereal or chloroform solution with a very small quantity of concentrated hydrochloric acid, the sides of the vessel become covered with crystals of the hydrochloride of the new base (*Apomorphinæ Hydrochloridum,* B.P.). These may be drained from the mother-liquor, washed with a little cold water, in which the salt is sparingly soluble, recrystallized from hot water, and dried on bibulous paper or over sulphuric acid. The formula, $C_{17}H_{17}NO_2,HCl$, may be derived from that of morphine by abstraction of the elements of water. "From solutions, solution of sodium bicarbonate throws down a precipitate which becomes green on standing and then forms a solution which is purple with ether, violet with chloroform, and bluish green with alcohol (90 per cent.). With dilute test-solution of ferric chloride it gives a deep red, and with nitric acid a blood-red coloration." A one per cent. aqueous solution of apomorphine hydrochloride constitutes the *Injectio Apomorphinæ Hypodermica*, B.P.

Other alkaloids exist in opium. In the preparation of morphine a considerable quantity of *narcotine*, $C_{22}H_{23}NO_7$, or $C_{19}H_{14}(OCH_3)_3NO_4$ (*Narcotina*, P.I.), an alkaloid of very weak basic properties, remains in the exhausted opium, and may be extracted by digesting in acetic acid, filtering, and precipitating by adding ammonia. It crystallizes in brilliant needles from alcohol or ether. The formula of its hydrochloride is $C_{22}H_{23}NO_7,HCl,H_2O$. By oxidation it yields *cotarnine* and an acid termed *opianic*. From the mother-liquors there have also been obtained *thebaine*, $C_{19}H_{21}NO_3$, *paparerine*, $C_{21}H_{21}NO_4$ (Hesse); $C_{20}H_{21}NO_4$ (Merck), *narceine*, $C_{23}H_{27}NO_8$, *cryptopine*, $C_{21}H_{23}NO_5$, *meconin*, $C_{10}H_{10}O_4$, *meconoisin*, $C_8H_{10}O_2$, *laudanine*, $C_{20}H_{25}NO_4$, *codamine*, $C_{20}H_{25}NO_4$, *gnoscopine*, $C_{22}H_{23}NO_7$, *pseudomorphine*, $C_{34}H_{36}N_2O_5$, *protopine*, $C_{20}H_{17}NO_5$, *laudanosine*, $C_{21}H_{27}NO_4$, *hydrocotarnine*, $C_{12}H_{15}NO_3$, *rhœadine*, $C_{21}H_{21}NO_6$, *meconidine*, $C_{21}H_{23}NO_4$, *lanthopine*, $C_{23}H_{25}NO_4$.

A little acetic acid also exists in opium (D. Brown).

Constitution of Morphine.—The opium alkaloids, like the cinchona alkaloids, have been attacked by many chemists in the hope that analytical or, in a sense, destructive investigation would lead to synthetical or constructive operations; and many interesting and promising results have been obtained. It is found that morphine is a tertiary base; it yields pyridine in several reactions, supporting the view that it is a pyridine derivative. By suitable oxidation, it yields picric acid, and by fusion with caustic alkali, protocatechuic acid, both which reactions indicate relationship to benzene. The nitrogen atom in morphine appears to have a methyl group attached to it. But the subject is not yet sufficiently developed for useful study by ordinary students of medicine or pharmacy.

QUESTIONS AND EXERCISES

Write some general formulæ of artificial alkaloids.—Name the substances represented by the following formulæ:—

$$\left.\begin{matrix}C_3H_7\\H\\H\end{matrix}\right\}N,\quad \left.\begin{matrix}C_3H_7\\C_3H_7\\H\end{matrix}\right\}N,\quad \left.\begin{matrix}CH_3\\C_2H_5\\C_5H_{11}\end{matrix}\right\}N,\quad \left.\begin{matrix}CH_3\\H\\H\end{matrix}\right\}N,\quad \left.\begin{matrix}CH_3\\CH_3\\H\end{matrix}\right\}N,\quad \left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\}N$$

Describe the treatment in cases of poisoning by alkaloids.—Give a process for the preparation of morphine hydrochloride. In what form does morphine occur in opium?—How is morphine acetate prepared?—What plan is adopted for preventing the decomposition of the official morphine solutions?—Mention the analytical reactions of morphine.—In addition to the reactions of morphine, what test may be employed in searching for opium in a liquid or semi-fluid material?—Describe the relation of morphine to codeine.—How is apomorphine prepared and what are its properties?

QUININE AND OTHER CINCHONA ALKALOIDS

Quinine ; $C_{20}H_{24}N_2O_2, 3H_2O$

Source.—Quinine and other alkaloids exist in the bark of various species of Cinchona and Remijia as *kinates*, or rather, *quinates*.* The official galenical preparations are made with the Succirubra or Red Cinchona Bark (*Cinchonæ Rubræ Cortex*, B.P.), from Cinchona succirubra, *Pavon*.

Extraction of the Mixed Alkaloids.—Mix two ounces of powdered cinchona bark with a quarter of its weight of slaked lime and a little water, and extract with benzolated amyl alcohol. (For a description of this operation, *see* the official assay of red cinchona bark, p. 789.) Shake the liquid product in a separating funnel with an ounce of water acidulated with sulphuric or hydrochloric acid. Draw off the aqueous liquid, which contains the alkaloids as acid salts, and add to it a slight excess of ammonia. Collect the precipitated alkaloids on a filter, wash, and dry by exposure to air, or in a desiccator over sulphuric acid. For the separation of alkaloids, an operation which should not be attempted at this stage of study, *see* "De Vrij's method," p. 792.

Quinine Sulphate (*Quininæ Sulphas*, B.P.) may be prepared by treating yellow cinchona bark with dilute hydrochloric acid, precipitating the resulting solution of quinine hydrochloride by means of caustic soda, and redissolving the precipitated quinine in the proper quantity of hot dilute sulphuric acid. Quinine sulphate crystallizes out on cooling in silky acicular crystals, having the formula $[(C_{20}H_{24}N_2O_2)_2H_2SO_4]_2$, $15H_2O$. In dry air it loses, by efflorescence, eleven-fifteenths of its water.

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* *Quinic acid*, $C_7H_{12}O_6$, occurs in cinchona, coffee, holly, ivy, oak, elm, etc. Heated it yields *hydroquinone*, $C_6H_4(OH)_2$. Oxidized it gives quinone, $C_6H_4O_2$, which is probably a di-ketone, $C_4H_4(CO)_2$ or $C_2H_2<\begin{matrix}CO\\CO\end{matrix}>C_2H_2$. The homologues of benzene yield other "quinones."

Quinine sulphate, the ordinary or so-called *neutral sulphate,* is only slightly soluble in water; on the addition of dilute sulphuric acid the so-called *acid sulphate* or *soluble sulphate,* $C_{20}H_{24}N_2O_2$, H_2SO_4, $7H_2O$, is formed, which is freely soluble. The latter salt may be obtained in large rectangular prisms. A soluble acid sulphate having the formula $C_{20}H_{24}N_2O_2$, $2H_2SO_4$, $7H_2O$, also exists. *Infusum Cinchonæ Acidum,* B.P., contains acid quinine sulphate.

The ordinary quinine sulphate is much more soluble in alcohol or alcoholic liquids than in water. An Ammoniated Tincture (*Tinctura Quininæ Ammoniata,* B.P.) is made by dissolving the sulphate in alcohol (60 per cent.) and adding a large excess of solution of ammonia. This tincture contains quinine itself, liberated from combination by, and dissolved by aid of the excess of, the ammonia. Quinine wine (*Vinum Quininæ,* B.P.) is a solution of quinine hydrochloride in orange wine. The remaining pharmacopœial preparations of quinine are the hydrochloride, acid hydrochloride, and the mixed iron, ammonium, and quinine citrates (*Ferri et Quininæ Citras,* B.P.), the well-known scale compound (*see* p. 174).

Quinine Hydrochloride (*Quininæ Hydrochloridum,* B.P.) may be prepared by neutralizing quinine with hydrochloric acid. Its formula is $C_{20}H_{24}N_2O_2,HCl,2H_2O$. It is soluble in about 34 parts of water at ordinary temperatures, the sulphate requiring 700 or 800. The two salts resemble each other in appearance, but the crystals of the hydrochloride are commonly somewhat larger than those of the sulphate. 175 grains of quinine hydrochloride dissolved in 1 pint of Tincture of Orange forms *Tinctura Quininæ,* B.P.

Acid Quinine Hydrochloride (*Quininæ Hydrochloridum Acidum,* B.P.) is "a white crystalline powder soluble in less than its own weight of water, yielding a somewhat acid liquid." Its formula is $C_{20}H_{24}N_2O_2,2HCl,3H_2O$.

Basic Quinine Citrate has the formula $(C_{20}H_{24}N_2O_2)_2,H_3C_6H_5O_7,5H_2O$. Other citrates contain three molecules of quinine to two of citric acid, and one of quinine to one of citric acid. *Quininæ Valerianas,* U.S.P., has the formula $C_{20}H_{24}N_2O_2,C_5H_{10}O_2,H_2O$.

Reactions.

1. To an acidulated solution of a quinine salt add fresh chlorine-water, shake, and then add solution of ammonia; a green coloration (*thalleioquin*) is produced. Bromine-water, or bromine-vapour, or solution of chlorinated lime may be used instead of chlorine.

2. Repeat the foregoing reaction, but prior to the addition of solution of ammonia add solution of potassium ferrocyanide; an evanescent red coloration is produced (Livonius and Vogel).

3. To an aqueous solution of a soluble quinine salt add solution of ammonium oxalate; a white crystalline precipitate of quinine oxalate, soluble in acids, is produced. If the solution to be tested be made from ordinary quinine sulphate, excess of the latter should be added to water very faintly acidulated with sulphuric acid, and the undissolved crystals removed by filtration.

4. A saturated aqueous solution of any neutral quinine salt is made by dissolving so much of the salt in hot water that some shall separate when the mixture has cooled to about 60° F. (15·5° C.). After standing for some time, filter. To the filtrate, ether which has been washed with water is added until a distinct layer of ether remains undissolved, and then ammonia in slight excess. After agitation and rest for fifteen minutes, all precipitated *quinine* will have redissolved.

Note.—In the case of *quinidine* salts well-defined crystals appear at the junction of the aqueous and ethereal layers, especially after standing. In the case of *cinchonidine* salts a thick layer of small crystals appears at once. In the case of *cinchonine* salts the undissolved alkaloid makes the ethereal layer nearly solid. In testing quinine for other alkaloids evaporate the aqueous solution to one-fifth.

5. Formation of Quinine Iodo-sulphate. Dissolve quinine sulphate in dilute alcohol slightly acidulated with sulphuric acid, and add an alcoholic solution of iodine; a black precipitate forms. Allow the precipitate to settle, pour away the liquid, wash once or twice with cold alcohol and then boil with alcohol; on cooling minute crystals separate. This iodo-sulphate is sometimes termed Herapathite, from the name of one of the chemists who discovered it (in 1852). The use of plates of this substance instead of tourmaline in certain forms of polarizing apparatus has been suggested, as they behave as tourmaline does towards light passing through them. Under the name of "iodide of hydriodate of quinine," Bouchardat described and used it in 1845. It is so slightly soluble in alcohol that by its means quinine can be fairly well separated from its admixture with the other cinchona alkaloids. According to Jörgensen it has the formula $4C_{20}H_{24}N_2O_2,3H_2SO_4,2HI,I_4,xH_2O$.

6. Prepare a saturated solution of ordinary quinine sulphate in water at about 60° F. (15·5° C.), and add to 5 volumes of that solution 7 volumes of solution of ammonia (sp. gr. 0·96). The alkaloid which is at first precipitated redissolves upon slight agitation if the quinine sulphate is free from anything but traces of other cinchona alkaloids. If, however, more than traces of quinidine, cinchonidine, and cinchonine salts be present, a permanent precipitate remains. This is Kerner's method of testing quinine sulphate for other cinchona alkaloids. It turns upon the fact that the solubility of the cinchona alkaloid sulphates in water is in the opposite order to the solubility of the alkaloids themselves in solution of ammonia.

Other characters.—Concentrated sulphuric acid dissolves quinine with production of only a faint yellow colour, which is not increased by warmth.——Quinine and its salts, heated on platinum foil, burn away entirely.——Most quinine salts when in solution have a beautiful blue fluorescence. They rotate the plane of polarization of light to the left.——Quinine is soluble in alcohol, ether, benzol, and chloroform. Ordinary quinine sulphate is insoluble in chloroform, and but slightly soluble in water. Its solubility in chloroform is increased by the presence in solution of quinidine and cinchonine sulphates (Prescott), and its solubility in water is decreased by the presence in solution of ammonium sulphate (Carles). The slight solubility of quinine sulphate and iodo-sulphate in water distinguishes quinine from the other cinchona alkaloids, including the "amorphous alkaloid," or quinoidine.

Quinidine, $C_{20}H_{24}N_2O_2$ (the *conquinine* or *conchinine* of Hesse), is an isomer of quinine. Its salts are fluorescent, and yield thalleioquin with chlorine- or bromine-water and ammonia. They rotate the plane of polarization of light to the right. Quinidine is insoluble in water and sparingly soluble in ether (*see* Quinine, 4th Analytical Reaction). It is soluble in alcohol, benzol, and chloroform. It is less soluble than quinine in ammonia, 5 volumes of a saturated aqueous solution of quinidine sulphate requiring 60 to 80 volumes of ammonia solution (sp. gr. 0·96). Its sulphate is more soluble in water and chloroform than quinine sulphate. Quinidine tartrate is soluble in water. The hydriodide is insoluble in water and dilute alcohol, and occurs as gritty crystals. The other cinchona alkaloid hydriodides, though more soluble than quinidine hydriodide, are sometimes precipitated from neutral concentrated solutions as amorphous or semi-liquid precipitates. These, however, are soluble in dilute alcohol. *Quinidinæ Sulphas*, U.S.P., has the formula $(C_{20}H_{24}N_2O_2)_2,H_2SO_4,2H_2O$.

Cinchonidine, $C_{19}H_{22}N_2O$.—The sulphate, $(C_{19}H_{22}N_2O)_2,H_2SO_4,3H_2O$, may be obtained from the mother-liquors from the crystallization of quinine sulphate. When perfectly pure, cinchonidine salts do not yield thalleioquin, and are not fluorescent. Even good commercial salts, however, nearly always give both reactions. Cinchonidine salts rotate the plane of polarization of light to the left. Cinchonidine is insoluble in water and nearly so in ether. (*See* Quinine, 4th Analytical Reaction.) It is soluble in alcohol, benzol, and chloroform. It is less soluble in ammonia solution than quinine, 5 volumes of a saturated aqueous solution of cinchonidine sulphate requiring about 80 volumes of ammonia solution (sp. gr. 0·96). It is true that cinchonidine is dissolved as readily as quinine if excess of saturated solution of ammonia is quickly mixed with the solution of the cinchonidine salt; but from such a solution cinchonidine soon crystallizes out, while quinine remains dissolved for many hours. Cinchonidine sulphate and hydriodide are soluble in water, but the sulphate, like quinine sulphate, is insoluble in chloroform. Cinchonidine tartrate is insoluble in water; and in this form cinchonidine is usually separated from neutral solutions containing the other cinchona alkaloids except quinine, the filtrate from the precipitate of tartrate yielding cinchonine on the addition of ammonia.

Cinchonine, $C_{19}H_{22}N_2O$, is an isomer of cinchonidine. The sulphate may be obtained from the mother-liquors from the crystallization of the quinine, cinchonidine, and quinidine sulphates, by adding caustic soda to precipitate the alkaloid, washing with alcohol until free from other alkaloids, dissolving in sulphuric acid, and, after purifying the solution with animal charcoal, allowing to crystallize. When quite pure, its salts are not fluorescent and do not yield thalleioquin, but as in the case of cinchonidine, most commercial specimens of cinchonine salts nearly always give both reactions. Cinchonine salts rotate the plane of polarization of light to the right. Cinchonine is insoluble in water and nearly so in ether. (*See* Quinine, 4th Analytical Reaction.) It is soluble in chloroform, benzol, and alcohol. Chloroform containing one-fourth of its weight of 95 per cent. alcohol dissolves cinchonine much more readily than either alcohol or chloroform alone. Cinchonine is insoluble in ammonia solution. Cinchonine sulphate, tartrate, and hydriodide are soluble in water, and the sulphate, like quinidine sulphate, is soluble in chloroform. In mixtures of cinchona alkaloids this alkaloid is precipitated by alkali after the others have been successively removed by ether, sodium tartrate, and potassium iodide.

"*Quinoidine*," "*chinoidine*," or the "*amorphous alkaloid.*" —Cinchona barks generally contain some alkaloid isomeric with quinine which, like quinine, is soluble in ether, but the ordinary sulphate and iodo-sulphate are not crystalline and are soluble. These salts are semi-solid resinous-looking substances. The iodo-sulphate is used in De Vrij's method for the separation of mixed alkaloids. Quinoidine is usually obtained along with the quinine, etc., extracted from the mixed alkaloids by ether, and remains in the mother-liquor, from which it is precipitated by an alkali.

Quinicine, and *cinchonicine,* are alkaloids produced by the action of heat on quinine or quinidine and on cinchonidine respectively. They, also, are isomers, Hesse says polymers, of the parent alkaloids. Both yield crystalline salts. *Quiniretin* is the name given to the brown or reddish-brown indifferent substance into which quinine in aqueous solution is converted when much exposed to light.

Quinamine, $C_{19}H_{24}N_2O_2$, is a fifth cinchona alkaloid obtained by Hesse in 1872 from the bark of *Cinchona succirubra.* Its solution is not fluorescent, and does not yield thalleioquin. Another alkaloid, *cinchamidine,* $C_{19}H_{24}N_2O$, detected by the same chemist, is identical with *hydrocinchonidine.*

Cupreine, $C_{19}H_{22}N_2O_2$, is an alkaloid discovered simultaneously by Howard and Hodgkin, by Paul and Cownley, and by Whiffen, in the bark of a Remijia (allied to Cinchona) and termed *cuprea* bark. It closely resembles quinine, but is sparingly soluble in ether. It may be converted into quinine by heating its sodium compound with methyl chloride; whence it appears that quinine is methyl-cupreine. The substance at first termed *homoquinine* or *ultraquinine* is a compound of cupreine and quinine, $C_{19}H_{22}N_2O_2$, $C_{20}H_{24}N_2O_2$, $4H_2O$.

Hydroquinine, $C_{20}H_{26}N_2O_2$, containing two more atoms of hydrogen than are present in the quinine molecule, is an alkaloid associated with quinine in minute quantity in cinchona bark. It remains in the mother-liquor when quinine sulphate is crystallized from an acid solution. Its characters are closely allied to those of quinine and its therapeutic action is similar. It was discovered by Hesse.

Constitution of the cinchona alkaloids. This is not yet clear, though great advances have been made. In the course of the investigations derivatives of quinoline have been obtained, which more or less resemble quinine; these are *kairine, kairoline,* and *thalline.*

Strychnine

Source.—Strychnine or strychnia, $C_{21}H_{22}N_2O_2$, exists, to the extent of about 1 per cent., in Nux Vomica (*Strychnos Nux-vomica*), also (Shenstone) in minute quantity in the bark of the Nux Vomica tree (false angostura bark) and to 1·0 or 1·5 per cent. in St Ignatius's bean (*Strychnos Ignatius*), partly, at least, in combination with strychnic or igasuric acid. Crow also found it in the bark of *S. Ignatius*.

Preparation.—Nux Vomica seeds, disintegrated by steaming, and, after drying, grinding in a coffee-mill, are exhausted with alcohol (90 per cent.), the latter is removed by distillation, the extract dissolved in water, colouring-matters and organic acids precipitated by adding lead acetate, the filtered liquid evaporated to a small bulk, the strychnine precipitated by means of ammonia, the precipitate washed, dried, and exhausted with the recovered alcohol, the latter again removed by distillation, and the residual liquid set aside to crystallize. Crystals of strychnine having formed, the mother-liquor (which contains the brucine of the seeds) is poured away, and the crystals of strychnine are washed with alcohol (to remove any brucine) and recrystallized. This alkaloid is official (*Strychnina*, B.P.).

Properties.—Strychnine occurs "in trimetric prisms; colourless and inodorous; very sparingly soluble in water, but communicating to it an intensely bitter taste; soluble in 150 parts of cold but in less of boiling alcohol (90 per cent.), and in 6 parts of chloroform; slightly soluble in cold absolute alcohol, but readily in 40 parts of boiling absolute alcohol, and nearly insoluble in ether." It forms salts with acids. The *sulphate* has the formula, $(C_{21}H_{22}N_2O_2)_2H_2SO_4$, $5H_2O$. It is soluble in about 40 parts of water. The *citrate* $(C_{21}H_{22}N_2O_2)_2,C_6H_8O_7$, $4H_2O$ (or $6H_2O$) dissolves, at 60° F., in about 40 parts of water and 115 parts of alcohol. The hydrochloride (*Strychninæ Hydrochloridum*, B.P.) has the formula $C_{21}H_{22}N_2O_2,HCl,2H_2O$, and is soluble in 35 parts of water. A number of crystalline, well-defined acids have been obtained from strychnine by oxidation.

Analytical Reactions of Strychnine.

1. Place a very small fragment of strychnine on a white plate, and near to it also a small piece of potassium bichrom-

ate; to each add one drop of concentrated sulphuric acid; after waiting a minute or so for the bichromate to fairly tinge the acid, mix the two drops of liquid by means of a glass rod; a beautiful purple colour is produced, quickly fading into a yellowish red. The following oxidizing agents may be used in place of the bichromate:—lead peroxide, black manganese oxide, potassium ferricyanide, or potassium permanganate.

This reaction is highly characteristic and delicate; a minute fragment of strychnine dissolved in much dilute alcohol, or, better, chloroform, and one drop of the solution evaporated to dryness on a porcelain crucible-lid or plate, yields a residue which immediately gives the purple colour on being oxidized in the manner directed.

2. Strychnine evaporated with nitric acid, and the residue moistened with alcoholic caustic potash and again evaporated, gives a yellow coloration, passing into reddish violet on addition of more caustic potash, and becoming yellow again on the addition of water. When atropine is treated in the same way a violet residue is obtained which becomes colourless on adding water.

Other Reactions.—Concentrated sulphuric acid does not act on strychnine, even at the temperature of boiling water, a fact of which advantage is taken in separating strychnine from other organic matter for the purposes of toxicological analysis.——Potassium thiocyanate produces, even in dilute solutions of strychnine, a white precipitate, which, under the microscope, is seen to consist of tufts of acicular crystals. ——Concentrated nitric acid does not colour strychnine in the cold, and on heating only turns it yellow.

The Physiological Test.—A small frog placed in an ounce of water to which $\frac{1}{100}$ of a grain of strychnine salt (acetate) is added, is, in two or three hours, seized with tetanic spasms on the slightest touch, and dies shortly afterwards.

Strychnine has an intensely bitter taste. Cold water dissolves only $\frac{1}{2000}$ part; yet this solution, even when largely diluted, is distinctly bitter. Alcohol is a somewhat better solvent. The salts of the alkaloid are more soluble. The official solution (*Liquor Strychninæ Hydrochloridi*, B.P.) contains 1 per cent. of strychnine hydrochloride, the solvent being three parts water and one part alcohol (90 per cent.).

BRUCINE, or BRUCIA, $C_{23}H_{26}N_2O_4$, $4H_2O$, is an alkaloid accompanying strychnine in Nux Vomica and St Ignatius's bean to the extent of about two per cent. It is readily distinguished by the intense red colour produced when nitric acid is added to it. *Igasurine*, once supposed to be a third alkaloid of nux vomica, has been shown by Shenstone to be only a mixture of brucine and strychnine.

Curarine, $C_{19}H_{26}N_2O$, the active principle of the arrow-poison termed *curari, urari, ourari, wourali*, or *woorara*, prepared from a *Strychnos*, resembles strychnine in giving a colour reaction on oxidation, but the colour is more permanent. Potassium iodide and cyanoplatinate do not with curarine afford precipitates which crystallize from alcohol like those of strychnine. Curarine, also, is readily soluble in water. Unlike strychnine, curarine is reddened by sulphuric acid; further it is not dissolved out by ether from an acid or alkaline liquid. *Curari* appears to vary much in strength and quality. It is probably a mixture of vegetable extracts. *Curine*, $C_{18}H_{19}NO_3$, also is said to be present.

Distinction of Brucine from Morphine.—The red coloration produced by the action of nitric acid on brucine is distinguished from that yielded with morphine, by the action of reducing agents (such as stannous chloride, sodium thiosulphate or hydrosulphide), which decolorize the morphine-red, but change that of the brucine to violet and green (Cotton). The solution of brucine in the nitric acid should be heated to the boiling-point, diluted with water, and the stannous chloride then added.

QUESTIONS AND EXERCISES

What alkaloids are more or less characteristic of the different varieties of cinchona bark? In what form do they occur?—By what method may quinine sulphate be obtained?—Give the characters of quinine sulphate.—Describe the tests for quinine.—Show how quinidine or cinchonine sulphates may be proved to be present in commercial quinine sulphate.—How are cinchonine and quinine distinguished from morphine?—Whence is strychnine obtained?—Describe the process for the isolation of strychnine.—Give the characters of strychnine.—Describe the tests for strychnine.—By what reagent is brucine distinguished from strychnine?—Distinguish between brucine and morphine.

ALKALOIDS OF LESS FREQUENT OCCURRENCE

Acalyphine is the well-marked alkaloid of *Acalypha* herb (B.P. Add. 1900) or *Rupi*, an expectorant used in place of senega.

Aconitine, Aconitina, or Aconitia, is an alkaloid obtained from Aconite (*Aconitum Napellus*) root (*Aconiti Radix*, B.P.). The alkaloid itself is only slightly soluble in water; it occurs in the plant in combination with a vegetable acid, forming a soluble salt.

Preparation.—Dunstan's process for the preparation of aconitine (*Aconitina*, B.P.) consists in dissolving out the alkaloid from the root with fusel oil, and shaking the solution with sulphuric acid, which takes up the aconitine; the acid is then freed from resin by shaking with chloroform, and the alkaloid liberated by ammonia in the presence of ether, which dissolves it as soon as it is liberated. The aconitine and benzaconine thus obtained are converted into hydrobromides, and separated by fractional crystallization.

Properties.—Aconitine usually occurs as a white powder. It has been obtained and studied in the crystalline state by Groves, Wright, Williams, and others. It is very slightly soluble in cold water, more so in hot, and much more soluble in alcohol, in ether, and in chloroform. "When rubbed on the skin, it causes a tingling sensation, followed by prolonged numbness." The thousandth part of a grain on the tip of the tongue produces, after a minute or so, a characteristic tingling sensation and numbness; larger quantities rubbed into the skin cause numbness. Sulphuric acid turns it of a yellowish and, afterwards, dirty violet colour.

According to Wright, who worked in conjunction with Groves and Williams, *Aconitum Napellus* yields, chiefly, crystalline *aconitine*, $C_{33}H_{43}NO_{12}$, with some crystalline *pseudaconitine*, $C_{36}H_{49}NO_{12}$. Dunstan and Umney found, in addition to aconitine ($C_{33}H_{45}NO_{12}$, Dunstan and Ince), *aconine*, and an amorphous alkaloid, *napelline* or *isaconitine*, the salts of which are also amorphous. Aconitine is readily hydrolysed into *aconine*, $C_{24}H_{39}NO_{10}$, and benzoic acid (Dunstan and Passmore). Aconine is physiologically inert; *benzaconine*, $C_{24}H_{38}(C_6H_5CO)NO_{10}$, is active but is not a poison; while *acetyl-benzaconine*, or *aconitine*, $C_{24}H_{37}(CH_3CO)(C_6H_5CO)NO_{10}$, is a most powerful poison. The constitution of aconine is not yet known.

The formula for aconitine adopted in the British Pharmacopœia is $C_{33}H_{45}NO_{12}$; according to Freund, aconitine is $C_{34}H_{47}NO_{11}$.

The tuberous roots of *Aconitum Ferox* and other species constitute the *bish* or *bikh* of India (*Aconiti Ferocis Radix*, P.I.). It chiefly contains the variety of aconitine termed *pseudaconitine*. Some of the aconitine of pharmacy is pseudaconitine.

According to Paul and Kingzett, the alkaloid of Japanese aconite has the formula $C_{29}H_{43}NO_{9}$, while Wright and Menke state that the formula is $C_{66}H_{88}N_2O_{21}$, and name it *japaconitine*.

Aconitum heterophyllum, *Atis*, or *Atees*, or *Wakhma* (*Aconiti Heterophylli Radix*, P.I.), contains no aconitine, but an alkaloid *atcesine* having the formula $C_{46}H_{74}N_2O_4$.

Unguentum Aconitinæ, B.P., is made by dissolving 10 grains of aconitine in oleic acid, and incorporating the solution with about an ounce of lard.

Aristolochine, an alkaloid, and *Aristolochin*, a substance having the physiological properties of aloin, also volatile oil, are obtained from some of the species of Aristolochia. The official drugs are *A. Serpentaria* or Virginia Snakeroot (*Serpentariæ Rhizoma*, B.P.) and *A. Indica* (*Aristolochia*, B.P. Add. 1900) or *Isarmul* (Hind.).

Aspidospermine, $C_{22}H_{30}N_2O_2$, is an alkaloid of *Quebracho blanco* bark (Fraude). Another alkaloid is *quebrachine*, $C_{21}H_{26}N_2O_3$ (Hesse). The latter chemist has isolated four other closely related alkaloids; also two from *Quebracho colorado* bark.

Atropine, or Atropia, $C_{17}H_{23}NO_3$ (*Atropina*, B.P.).—This alkaloid was formerly considered to exist ready formed in the Belladonna, or Deadly Nightshade (*Atropa Belladonna*) (*Belladonnæ Folia*; *Belladonnæ Radix*, B.P.), as soluble acid atropine malate. But the observations of Messrs Schering and the researches of Will indicate that it is not atropine but an isomer of atropine, namely hyoscyamine, which is the alkaloid chiefly and often solely present, and that the treatment with alkali, during the process of extraction, converts the hyoscyamine into atropine. Hyoscyamine solutions rotate the plane of polarization of light to the left; atropine has no optical rotatory power. Both possess the property of dilating the pupil of the eye. *See* also HYOSCYAMINE.

Preparation.—Atropine may be obtained by exhausting the root with alcohol, precipitating the acid and some colouring-matter by adding lime, filtering, adding sulphuric acid to form atropine sulphate (which is somewhat less liable to decomposition during subsequent operations than the alkaloid itself), recovering most of the alcohol by distillation, adding water to the residue, and evaporating till the remaining alcohol is removed; solution of potassium carbonate is then poured in till the liquid is nearly, but not quite, neutral, whereby resinous matter is precipitated: the latter is filtered off, excess of potassium carbonate then added, and the liberated atropine dissolved out by shaking the liquid with chloroform. The latter solution, having subsided, is separated, the chloroform recovered by distillation, the residual atropine dissolved in warm alcohol, colouring-matter removed by digesting the liquid with animal charcoal, and the solution filtered, evaporated, and set aside to deposit crystals.

Atropine is sparingly soluble in water, the liquid having an alkaline reaction It is more soluble in alcohol and ether.

Tests.—With chlorauric acid, atropine solutions yield a yellow precipitate. One drop of a dilute aqueous solution of atropine (two grains to the ounce) powerfully dilates the pupil of the eye.

Baryta water decomposes atropine into *tropine*, $C_8H_{15}NO$, and *tropic acid*, $C_9H_{10}O_3$, a molecule of water being absorbed:

$$C_{17}H_{23}NO_3 + H_2O = C_8H_{15}NO + C_9H_{10}O_3.$$

Hence atropine would seem to be the tropine ester of tropic acid. By heating tropine and tropic acid in sealed tubes Ladenburg has succeeded in reproducing atropine, and has thereby rendered possible the synthesis of this alkaloid from its elements. Similarly a number of new alkaloids, known as *tropeïnes* and analogous to atropine, have been obtained by treating tropine with other acids. One of these is *homatropine* (*see* below) which is the tropine ester of mandelic acid. By removing the elements of water from tropine, Ladenburg obtains *tropidine*, $C_8H_{13}N$, closely related to ecgonine (p. 621) and anhydro-ecgonine.

Tropine, when neutralized with mandelic acid, and the salt so formed heated with hydrochloric acid, yields homatropine, the hydrobromide of which, $C_{16}H_{21}NO_3,HBr$, is official (*Homatropinæ Hydrobromidum*, B.P.). Discs of homatropine are also official (*Lamellæ Homatropinæ*, B.P.). Homatropine hydrobromide is a white crystalline powder or aggregation of minute trimetric crystals, soluble in 6 parts of cold water, and in 133 of absolute alcohol. The dilute aqueous solution powerfully dilates the pupil of the eye. A 2 per cent. aqueous solution is not precipitated by the cautious addition of solution of ammonia previously diluted with twice its volume of water [distinction from atropine]. About a tenth of a grain moistened with two minims of nitric acid and evaporated to dryness on the water-bath yields a residue which is coloured yellow by an alcoholic solution of caustic potash [distinction from atropine, hyoscine, and hyoscyamine]. If about a tenth of a grain be dissolved in a little water and the solution be made alkaline with ammonia and shaken with chloroform, the separated chloroform will leave on evaporation a residue which will turn yellow and finally brick-red when warmed with about fifteen minims of a solution of two grains of mercuric chloride in a hundred minims of proof spirit; for Gerrard, Schweissinger, and Flückiger have observed that homatropine (Ladenburg's oxytoluyltropeine, which is a physiologically similar but less powerful and therefore sometimes more useful alkaloid than atropine), like hyoscyamine and atropine, has unusually powerful alkaline properties, precipitating mercuric oxide from mercuric solutions, reddening phenolphthalein, and, with the aid of heat, blackening calomel. No other ordinary alkaloids are so powerfully alkaline.

In the so-called Japanese belladonna (*Scopola Japonica*) there occurs *scopoleine*, an alkaloid resembling, but more powerful than, atropine (Eykman); but Schmidt considers that only atropine, hyoscyamine and hyoscine are present. *See* p. 625.

Preparations.—The alkaloid itself (*Atropina*); its sulphate (*Atropinæ Sulphas*), a colourless powder soluble in water (made by neutralizing atropine with sulphuric acid); discs (*Lamellæ Atropinæ*), each containing $\frac{1}{5000}$ grain of atropine sulphate (applied by placing between the eyelid and the eye); a solution (*Liquor Atropinæ Sulphatis*, 1 per cent.); and an ointment (*Unguentum Atropinæ*, nearly 10 grains per ounce), are official in the British Pharmacopœia.

Extractum Belladonnæ Liquidum, B.P., is obtained from belladonna root, and is standardized to contain 0·75 per cent. of total alkaloid. *Extractum Belladonnæ Alcoholicum* and *Extractum Belladonnæ Viride* are also official.

The fluorescence of alkaline solutions of extract of belladonna is caused by *chrysatropic acid* (Kunz), which appears to be identical with the fluorescent *scopoletin,* $C_{10}H_8O_4$, found in Japanese belladonna by Eykman.

BAPTITOXINE.—Schrœder gives this name to a poisonous alkaloid in *Baptisia tinctoria,* wild indigo, in which he also finds the glucosides *baptisin* and *baptin.*

BEBERINE, BEBIRINE, or BIBIRINE, $C_{18}H_{21}NO_3$, is an alkaloid in the bark of Bebeeru, or Bibiru (*Nectandra Rodiæi*).

Beberine sulphate, $(C_{18}H_{21}NO_3)_2$, H_2SO_4, may be prepared by exhausting the bark with water acidulated with sulphuric acid, concentrating, removing most of the acid by adding lime, filtering, precipitating the alkaloid with ammonia, filtering, drying, dissolving in alcohol (in which some accompanying matters are insoluble), recovering most of the alcohol by distillation, neutralizing with dilute sulphuric acid, evaporating to dryness, dissolving the residual sulphate in water, evaporating to the consistence of a syrup, spreading on glass plates, and drying the product at 140° F. (60° C.). Thus obtained, it occurs in dark-brown translucent scales, yellow when powdered, strongly bitter, soluble in water and in alcohol. It is probably a mixture of beberine sulphate, nectandrine sulphate, and other alkaloidal sulphates.

Tests.—Alkalies give a pale-yellow precipitate of beberine when added to an aqueous solution of a salt of the alkaloid; the precipitate is soluble in ether. With potassium bichromate and sulphuric acid, beberine gives a black resin, and with nitric acid a yellow resin.

Buxine, from the bark of *Buxus sempervirens; pelosine, or cissampeline,* from the dried root (*Pareiræ Radix,* B.P.) of *Chondrodendron tomentosum* and of *Cissampelos Pareira* (*Cissampelos,* B.P. Add. 1900); and *paricine,* from a false Para cinchona-bark, are probably identical with beberine (Flückiger).

Nectandrine ($C_{40}H_{46}N_2O_8$, $4H_2O$).—Maclagan and Gamgee discovered this alkaloid in Bebeeru-wood. It differs from beberine in fusing when placed in boiling water, in being much less soluble in ether, and in giving with concentrated sulphuric acid and black manganese oxide a beautiful green and then a violet coloration. They considered that two other alkaloids exist in Bebeeru-wood.

BERBERINE, $C_{20}H_{17}NO_4$, is an alkaloid existing in several plants of the natural order *Berberidaceæ* (three species yield *Indian Barberry, Berberis Cortex*, P.I., one, *B. aristata*, affording the dried stem termed *Berberis* in the B.P. Add. 1900), in Calumba-root (*Calumbæ Radix*, B.P.), in the root of *Coptis Teeta* or *Mishmi Bitter* (*Coptidis Radix*, P.I.), an Indian tonic, in the dried stem of *Coscinium fenestratum* (*Coscinium*, B.P. Add. 1900), and in many other yellow woods. *Hydrastis Canadensis* or *Golden Seal*, contains berberine, though a second alkaloid, *hydrastine*, related to narcotine and to papaverine, and even a third, are said to be present, all, in Perkin's opinion, benzene derivatives of iso-quinoline. Hydrastine acid tartrate, $C_{21}H_{21}NO_6$, $C_4H_6O_6$,$4H_2O$, has been obtained in the crystalline form. The dried rhizome and rootlets are official, *Hydrastis Rhizoma*, B.P., and these are the source of the *Extractum Hydrastis Liquidum*, B.P., and *Tinctura Hydrastis*, B.P. The root of *Berberis vulgaris* contains berberine and *oxyacanthine*, $C_{19}H_{21}NO_3$, (Rüdel), as well as *berbamine*, $C_{18}H_{19}NO_3$, (Hesse). *Xanthorrhiza apiifolia*, an old American tonic, and, apparently, *Xanthoxylon Fraxineum*, or Prickly Ash, also contain berberine. The rhizome of *Menispermum Canadense, Yellow Parilla*, or *Canadian Moonseed*, contains, according to Maisch, a colourless alkaloid as well as berberine. The colour of the tissues of these plants is apparently due to berberine; for the alkaloid itself is remarkable for its beautiful yellow colour.

Preparation.—Berberine is readily extracted by boiling the raw material with water, evaporating the strained liquid to a soft extract, digesting the residue in alcohol, recovering the alcohol by distillation, boiling the residue with dilute sulphuric acid, filtering and setting aside; berberine acid sulphate, $C_{20}H_{17}NO_4$, H_2SO_4, which is sparingly soluble, separates out and may be purified by recrystallization from hot water. The alkaloid itself is obtained by shaking lead hydroxide with a hot aqueous solution of berberine acid sulphate (Procter).

Tests.—When a dilute solution of iodine and potassium iodide is added to a solution of any salt of berberine in hot alcohol, large excess of iodine being carefully avoided, brilliant green spangles of a periodide, $C_{20}H_{17}NO_4I_2,HI$, are deposited. The reaction is sufficiently delicate to form, according to Perrins, an excellent test for the presence of berberine. This iodo-compound polarizes light, and has other analogies with herapathite.

Berberine itself is not official, but plants in which it occurs are used as medicinal agents in all parts of the world.

CAFFEINE, or THEINE, or GUARANINE (Methyl-theobromine) (*Caffeina*, B.P.), $C_8H_{10}N_4O_2$, H_2O.—This alkaloid occurs in Tea, 2 to 4·5 per cent.; Coffee, 1·2 per cent.; Maté or Paraguay Tea, 0·2 to 2 per cent.; Guarana, 5 per cent.; and the Kola-nut, 0·5 per cent. Infusions and preparations of these vegetable products are used, chiefly as beverages, by three-fourths of the human race. It is remarkable that the instinct of man, even in his savage state, should have led him to select, as the basis of beverages in such common use, just the four or five plants which out of many thousands are the only ones, so far as we know, containing caffeine.

Caffeine is volatile. Considerable quantities may be collected by condensing the vapours evolved during the roasting of coffee on the large scale. A decoction of tea, from which astringent and colouring-matters have been precipitated by solution of lead subacetate, and which has then been acidulated with sulphuric acid and well washed with chloroform, the latter fluid evaporated, and the residue dried at 100° C., yields an average of a little over 3 per cent. (of the tea) of anhydrous caffeine. It may be crystallized from alcohol or by sublimation. It forms salts with acids (*Caffeinæ Citras*, B.P., $C_8H_{10}N_4O_2$, $C_6H_8O_7$); they are decomposed by water.

Caffeinæ Citras Effervescens, B.P., is made by mixing caffeine citrate with tartaric and citric acids, sodium bicarbonate, and sugar, heating and stirring until the mixture assumes a granular character.

Test.—Concentrated nitric acid, or, better, a mixture of potassium chlorate and hydrochloric acid, rapidly oxidizes caffeine, forming compounds which with ammonia yield a beautiful purple-red colour, resembling the murexid obtained under similar circumstances from uric acid; the oxidation must not be carried too far. Caffeine boiled with caustic potash yields methylamine.

The main physiological action of caffeine on the system is a stimulating one especially affecting heart-muscle.

The commercial value of tea depends upon its appearance and on the flavour and odour of the infusion, the percentage of caffeine not varying much. China tea contains rather less caffeine and much less astringent matter than tea from Ceylon or India. Tea infused in boiling water for five minutes yields somewhat more than half its caffeine to the fluid.

Graphic formula for Caffeine.—See p. 630.

Capsicine.—Felletár obtained from Capsicum-fruit (*Capsici Fructus*, B.P.), which when ground forms *Cayenne Pepper*, a volatile alkaloid having the smell of conine. Thresh has obtained crystalline hydrochloride and sulphate. The latter chemist has also succeeded in isolating the active principle of capsicum, which he has termed *capsaicin*, $C_9H_{14}O_2$, a crystalline non-alkaloidal excessively acrid substance. Its exact chemical character is not yet made out, but Micko regards it as a nitrogen compound possessing a slightly acid phenolic character and gives it the formula $C_{18}H_{28}NO_3$. According to Thresh a similar very pungent principle occurs in ginger (gingerol) and in grains of paradise (paradol), bodies probably isomeric with capsaicin. (*See* also *Capsicin*, p. 553.)

Carpaine, $C_{14}H_{25}NO_2$, occurs in *Carica papaya.*

Cephæline, $C_{14}H_{20}NO_2$, is an alkaloid found in the root of *Cephælis Ipecacuanha;* about one-third of the total alkaloid in the root is cephæline, the remainder being principally emetine (a third alkaloid is present in small quantity). Cephæline is not equal to emetine as an expectorant, but is superior as an emetic; it is rapidly decomposed when boiled with alcohol. *See* also Emetine.

Cocaine, $C_{17}H_{21}NO_4$, is an alkaloid of *Erythroxylon Coca*, the leaves of which (*Cocæ Folia*, B.P.) act powerfully as a restorative to the human system. The alkaloid itself and its hydrochloride are both official (*Cocaina*, B.P., and *Cocainæ Hydrochloridum*, B.P.); also a 10 per cent. solution of the latter (*Injectio Cocainæ Hypodermica*, B.P.), preserved by aid of salicylic acid; discs (*Lamellæ Cocainæ*, B.P.), each containing $\frac{1}{50}$ grain; a lozenge (*Trochiscus Krameriæ et Cocainæ*, B.P.), and an ointment (*Unguentum Cocainæ*, B.P.). Cocaine and its salts may be prepared by agitating with petroleum spirit a concentrated, acidulated, aqueous extract of the leaves made alkaline with sodium carbonate, well shaking the separated spirit with acidulated water, treating the separated acid liquid with ether and excess of sodium carbonate, washing out the alkaloid from the ether with water containing hydrochloric acid, and finally evaporating the resulting aqueous solution of the hydrochloride to the crystallizing point. Cocaine may be precipitated with ammonia and recrystallized from alcohol, ether, or warm benzene. It melts at 204·8° to 208·4° F. (96° to 98° C.). From this pure cocaine the pure and very soluble hydrochloride may be prepared by neutralizing with hydrochloric acid and crystallizing.

Prolonged contact of cocaine with hot water, acids, alkalies, or even alcohol, is undesirable, as cocaine readily breaks up into benzoyl-ecgonine, and methyl alcohol, $C_{17}H_{21}NO_4 + H_2O = C_{16}H_{19}NO_4 + CH_3OH$, benzoyl-ecgonine afterwards yielding ecgonine and benzoic acid, $C_{16}H_{19}NO_4 + H_2O = C_9H_{15}NO_3 + C_7H_6O_2$. Other bases occur in coca besides cocaine. Paul and Cownley, also Giesel, find *cinnamyl-cocaine.* Hesse finds two amorphous bases which he names *cocamine* and *cocaidine.* Liebermann finds several bases, one of which is poisonous, namely, *isatropyl-cocaine,* $C_{19}H_{23}NO_4$ (identical with Hesse's cocamine), containing an isatropyl group in place of the benzoyl group in ordinary cocaine. All these bases are easily hydrolyzed, yielding ecgonine; the latter with benzoic anhydride yields benzoyl-ecgonine; and this with methyl iodide, yields benzoyl-methyl ecgonine, or ordinary cocaine. A series of "cocaines" can be produced by introducing other groups into ecgonine instead of the benzoyl groups.

Another alkaloid (benzoyl-pseudo-tropeine), yielding instead of ecgonine a compound isomeric with tropine, also occurs in coca (Giesel; Liebermann).

Cocaine hydrochloride occurs in colourless acicular crystals soluble in water, chloroform, alcohol, amyl alcohol; very slightly in ether; not readily decomposed even when boiled in water. The free alkaloid is readily decomposed by water, especially when the solution is warmed. The solution in water has a bitter taste; gives a purple precipitate with permanganates; and a white precipitate with ammonia. Its solution produces on the tongue a tingling sensation, followed by numbness. The aqueous solution dilates the pupil of the eye. It gives no colour to cold concentrated acids, but chars with hot sulphuric acid. Evaporated to dryness on a water-bath with nitric acid, and treated with alcoholic potash, it develops an odour resembling peppermint. Besides its action as a restorative when taken internally, cocaine brought into contact with the mucous membrane of the eye, mouth, throat, etc., or when injected, produces local anæsthesia. According to Squibb, good coca leaves yield 0·5 per cent. of cocaine. Cocaine may be detected in presence of other alkaloids by giving a yellow precipitate of cocaine chromate with either potassium chromate or chromic acid *in presence of free hydrochloric acid.*

COLCHICINE, the active principle of *Colchicum autumnale* (*Colchici Cormus*, B.P.; *Colchici Semina*, B.P.), is said to be an alkaloid, though some investigators think it has more of the characters of a neutral substance. Hertel states that ebullition with acidulated water converts it into *colchiceine* and methyl alcohol. Zeisel says it may be crystallized from chloroform, and offers the following formulæ for it and its derivative; *colchicine*, $C_{21}H_{22}(OCH_3)NO_5$; *colchiceine*, $C_{21}H_{22}(OH)NO_5$. The most active medicinal preparation is an extract made from the *fresh* seeds by digestion in large volumes of alcohol (of at least 90 per cent.) and subsequent digestion of the marc in hot water. The extracts left on evaporating the two liquids separately are to be carefully mixed (Mols).

CONINE, CONIA, CONYLIA, CONICINE, or CICUTINE, $C_8H_{17}N$, *a-normal-propyl-piperidine*, $C_5H_{10}N(C_3H_7)$. This alkaloid is a volatile liquid, occurring in Hemlock (*Conium maculatum*) in combination with an acid (malic ?). It is not official. According to Petit its boiling-point is 170° C., and its density 0·846. It forms crystalline salts.

Preparation.—Conine may be obtained by distilling hemlock-fruit (*Conii Fructus*, B.P.) with water rendered slightly alkaline with caustic soda or potash, or by similarly treating the fresh juice of the leaves. The crude alkaloid is a yellow oily liquid, floating on the water that distils over; by redistillation it is obtained colourless and transparent. Hemlock-leaves (*Conii Folia*, B.P.) are official.

The salts of conine are odourless, but when moistened with solution of an alkali yield the alkaloid, the strong odour of which, at once recalling hemlock, is characteristic.

Tests.—Sulphuric acid turns conine purplish red, changing to olive-green; nitric acid a blood-red; chlorauric acid produces a yellowish-white precipitate, chloroplatinic acid no precipitate in aqueous solutions.

Hemlock also contains *methyl conine*, $(C_8H_{16})CH_3N$ (Kekulé and Von Planta), and *conhydrine*, $C_8H_{17}NO$. The latter by dehydration yields a base, $C_8H_{15}N$.

According to Schiff, conine, isomeric, at least, with the natural alkaloid, may be produced artificially by action of ammonia on butyric aldehyde and destructive distillation of the resulting compound. Ladenburg has produced conine, identical with the natural alkaloid, from α-picoline. Conine may now therefore be said to be a product of organic synthesis, producible from its elements.

CORYDALINE, $C_{22}H_{27}NO_4$, occurs together with several other alkaloids in the tubers of *Corydalis cava*, in which it was discovered by Wackenroder in 1826. It forms colourless prismatic crystals which are practically insoluble in cold water, readily soluble in ether and chloroform, and sparingly soluble in alcohol. The crystals melt at 134·5° C. Both crystals and solutions quickly assume a yellow colour on exposure to light or on heating. The alkaloid forms a number of salts, some of which crystallize well.

CUSPARINE, $C_{20}H_{19}NO_3$, with *cusparidine*, $C_{19}H_{17}NO_3$, and *galipine*, $C_{20}H_{21}NO_3$, are alkaloids occurring in the bark of *Galipea cusparia*, or true Angostura Bark (*Cuspariæ Cortex*, B.P.). The bitter principle, *angosturin*, is not an alkaloid.

CYTISINE or ULEXINE, $C_{10}H_{14}N_2O$, is an alkaloid found in laburnum and furze, and is identical with *sophorine*, from *Sophora tomentosa*.

DATURINE.—*See* HYOSCYAMINE.

DELPHINE, or DELPHININE and DELPHINOIDINE are the poisonous alkaloids of Stavesacre (*Delphinium Staphisagria*). The powdered seeds of the plant are employed to kill the *pediculi* of animals. The seeds (*Staphisagriæ Semina*, B.P.) contain about 25 per cent. of oil. *Unguentum Staphisagriæ*, B.P., contains about 5 per cent. of the oil.

DITAMINE, $C_{16}H_{19}NO_2$ (Jobst and Hesse), is an alkaloid of "Dita," or bark of *Echites scholaris* or *Alstonia scholaris* (*Alstonia*, B.P. Add. 1900; *Alstoniæ Cortex*, P.I., or *Chattian*

—Hind.), a reputed febrifuge. Others are *echitamine* or *ditaine* and *echitenine*. Oberlin and Schlagdenhauffen state that the allied *Alstonia constricta* (the bark of which is said to have advantages over the hop as a dietetic bitter) contains a crystalline alkaloid, *alstonine* and uncrystallizable *alstonicine*. Alstonine seems to be allied to strychnine.

DUBOISINE.—*See* HYOSCYAMINE.

EMETINE, $C_{15}H_{22}NO_2$.—This alkaloid is one of the active principles of the root of *Psychotria Ipecacuanha* (*Ipecacuanhæ Radix*, B.P.). It occurs to the extent of 1 to 2 per cent. in the root (less in the stems) in combination with ipecacuanhic acid. The nitrate is peculiarly slightly soluble in water (Lefort). In *Pulvis Ipecacuanhæ Compositus*, B.P., or Dover's Powder (Powdered Ipecacuanha, 1 part; Powdered Opium, 1 part; and Potassium Sulphate, 8 parts), minute division of the active ingredients is promoted by prolonged trituration with the potassium sulphate, which is a very hard salt. In the U.S. Pharmacopœia milk sugar is the diluent. Liquid Extract of Ipecacuanha (*Extractum Ipecacuanhæ Liquidum*, B.P.), contains 2 to 2¼ grains of the alkaloids of the root in 110 minims. *Ipecacuanha Wine* (*Vinum Ipecacuanhæ*, B.P.) is a mixture of 1 part by volume of Liquid Extract of Ipecacuanha with 19 of sherry. *Acetum Ipecacuanhæ*, B.P., is a mixture of 1 part by volume of the Liquid Extract with 2 of alcohol (90 per cent.) and 17 of dilute acetic acid. Cephæline (½ per cent. in Brazilian and 1¼ per cent. in Columbian, according to Paul and Cownley) and small quantities of a third alkaloid, are also found in ipecacuanha.

The Indian substitute for ipecacuanha is the dried leaf (*Tylophoræ Folia*, B.P. Add. 1900, and P.I.) of *Tylophora asthmatica*. Its active principle has not been satisfactorily determined, but would seem to be the alkaloid *tylophorine* (Hooper).

GELSEMINE, $C_{22}H_{38}N_2O_4$.—This is one of the alkaloids of *Gelsemium nitidum*, or Carolina Yellow Jasmine (*Gelsemii Radix*, B.P.), in the tissues of which plant the *gelseminic acid* of Wormley, and *æsculin*, $C_{15}H_{16}O_9$, the fluorescent glucoside of the Horse Chestnut and of many other plants, are also present. Like strychnine, gelsemine is not apparently affected by concentrated sulphuric acid. Nitric acid does not colour it. A mixture of sulphuric acid and black manganese oxide colours it a crimson red, changing to green. In *Gelseminum elegans,* Crow finds an allied alkaloid which does not resist the action of sulphuric acid. *Gelseminine,* $C_{22}H_{26}N_2O_3$, is another *Gelsemium* alkaloid, said to be more powerful than gelsemine.

GRINDELINE is the name given by Fischer to a bitter crystalline alkaloid he extracted from *Grindelia* (*robusta*), U.S.P. (*Grindelia,* B.P. Add. 1900, from *G. squarrosa* and *G. robusta.*) The plant also contains a resin and a volatile oil.

HOMATROPINE.—*See* ATROPINE.

HYDRASTINE.—*See* BERBERINE.

HYOSCINE or SCOPOLAMINE.—Besides hyoscyamine, Ladenburg finds in henbane some *hyoscine,* $C_{17}H_{21}NO_4$, identical with scopolamine from *Scopola atropoides* and *S. carniolica.* Hyoscine hydrobromide is official (*Hyoscinæ Hydrobromidum,* B.P.).

HYOSCYAMINE, $C_{17}H_{23}NO_3$, occurs in the leaves (*Hyoscyami Folia,* B.P.), and other parts of Henbane (Hyoscyamus niger), Belladonna, Stramonium, and various species of Scopola ; also (Dymond) in Lettuce. It forms brilliant colourless needles. Its salts also are crystalline. Its effect on the eye is similar to that of atropine. The researches of Ladenburg show that hyoscyamine is the tropate of an alkaloid isomeric with tropine. The sulphate is official (*Hyoscyaminæ Sulphas,* B.P.). (*See* ATROPINE.)

The alkaloids in *Datura Stramonium,* or Thornapple (*Stramonii Folia,* B.P., and *Stramonii Semina,* B.P.), *Dhatura* (*Datura alba ; Daturæ Folia et Semina,* P.I.), the leaves of *Datura fastuosa* and *D. Metel* (*Daturæ Folia,* B.P. Add. 1900), and the seeds of *Datura fastuosa* (*Daturæ Semina,* B.P. Add. 1900), and in *Duboisia Myoporoides,* were formerly supposed to be distinct alkaloids, called respectively *Daturine* and *Duboisine,* but are identical with hyoscyamine, which is isomeric with atropine (Ladenburg). According to Schmidt, the alkaloid of *Duboisia myoporoides* is sometimes hyoscyamine and sometimes hyoscine or scopolamine. Pseudohyoscyamine, $C_{17}H_{23}NO_3$, also occurs in the latter plant. Bees which sip from the flowers of stramonium are said to deposit poisonous honey.

Hyoscyamine melts when heated to between 108° and 109° C., and then is soon converted into atropine. Its solutions in alcohol or ether are stable, but the presence of a very minute amount of fixed caustic alkali, or of alkali-metal carbonate, causes its complete conversion into atropine. With chlorauric acid its salts give a yellow crystalline precipitate, soluble in boiling water acidulated with hydrochloric acid, and again deposited, as the solution cools, in brilliant, golden-yellow scales.

JABORANDINE and JABORINE.—*See* PILOCARPINE.

JERVINE, $C_{26}H_{37}NO_3$, occurs in *Veratrum album*, White Hellebore, and *V. viride*,* American White Hellebore. Its salts are much less soluble in water than those of veratrine. According to Bullock, *Veratrum viride* contains another alkaloid—*veratroidine;* and, according to Mitchell, *Veratrum album* also contains another alkaloid which he terms *veratralbine.* Tobien gives the formula of Jervine as $C_{27}H_{47}N_2O_8$, and of veratroidine as $C_{51}H_{78}N_2O_{16}$, or $C_{24}H_{37}NO_7$. According to Wright, *Veratrum album* contains jervine, $C_{26}H_{37}NO_3$; pseudojervine, $C_{29}H_{43}NO_7$; rubijervine, $C_{26}H_{43}NO_2$; veratralbine, $C_{28}H_{43}NO_5$; and traces of veratrine, $C_{37}H_{53}NO_{11}$. The same author finds *Veratrum viride* to contain jervine, pseudojervine, cevadine, $C_{32}H_{49}NO_9$, rubijervine and traces of veratrine and veratralbine. Pehkschen finds jervine, pseudojervine, and veratroidine, while Salzberger, besides jervine, rubijervine, and pseudojervine, finds protoveratrine, $C_{32}H_{51}NO_{11}$, and protoveratridine, $C_{26}H_{45}NO_8$. Salzberger confirms Wright and Luff's formula for jervine.

LOBELINE.—A volatile fluid alkaloid first isolated from the dried flowering herb *Lobelia inflata* (*Lobelia*, B.P.) by Procter. In the pure state it is inodorous, impure it smells slightly, but mixed with ammonia emits a strong and characteristic smell of the plant. With acids it forms salts. A solid alkaloid also is said to be present.

LUPULINE is stated by Greismayer to be a liquid volatile alkaloid contained in the Hop, *Humulus Lupulus* (*Lupulus*, B.P.).

NECTANDRINE.—*See* BEBERINE.

NICOTINE, $C_{10}H_{14}N_2$.—This is a volatile liquid alkaloid, forming the powerful active principle of Tobacco (*Nicotiana*

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* The name *Green Hellebore* is sometimes applied to this drug, but properly belongs to *Helleborus viridis* (*see* "Helleborin" p. 582), which is used medicinally in some parts of Europe.—*Hanbury.*

Tabacum), nicotine malate and citrate being the forms in which it occurs in the leaf. Its odour is characteristic; like conine, it yields a precipitate with chlorauric acid, but, unlike that alkaloid, its aqueous solutions yield a yellowish white precipitate with chloroplatinic acid. It is not official. It is also contained in *Pituri*, a drug "chewed by the natives of some parts of Australia as a stimulant narcotic," though, according to Liversedge, the latter alkaloid may have the formula $C_{12}H_{16}N_2$.

Physostigmine, or Eserine (from *Esere*, the name of the ordeal poison of the bean at Calabar), $C_{15}H_{21}N_3O_2$.—An alkaloid of melting-point 106° C., obtained from the Calabar Bean (*Physostigmatis Semina*, B.P.), the seed of *Physostigma venenosum* (Jobst and Hesse), by dissolving the alcoholic extract in water, filtering, adding sodium bicarbonate, shaking the mixture with ether, and evaporating the ethereal liquid. The sulphate is official (*Physostigminæ Sulphas*, B.P.). It occurs "in yellowish-white minute crystals, becoming red by exposure to air and light, having a bitter taste, highly deliquescent, very soluble in water, and soluble in alcohol (90 per cent.). The aqueous solution is neutral to litmus, and affords the reactions characteristic of sulphates; when shaken with dilute solution of potassium hydroxide it becomes red; and when mixed with solution of ammonia and evaporated to dryness on a water-bath, it leaves a bluish residue, the solution of which in very dilute acids is dichroic, being red by reflected and blue by transmitted light." A trace of it powerfully contracts the pupil of the eye and is applied in the form of discs (*Lamellæ Physostigminæ*, B.P.); a small quantity is highly poisonous. Eber states that physostigmine, by action of acids, etc., takes up the elements of water and becomes *eseridine*, $C_{15}H_{23}N_3O_3$, melting-point 132° C., an alkaloid one-sixth the strength of physostigmine and occurring to some extent in the Calabar bean itself. Ehrenberg finds, also, *eseramine*, $C_{16}H_{25}N_4O_3$ (melting-point 238° C., physiologically inactive), and gets *eseroline* as a derivative of physostigmine.

Pilocarpine is, apparently, the active principle of the diaphoretic and sialogogue *Pilocarpus Jaborandi* (*Jaborandi Folia*, B.P.). The occurrence of an alkaloid in this plant was first announced by Hardy, followed almost immediately by Byasson. A crystalline nitrate and hydrochloride were first obtained by Gerrard. The leaves also yield an essential oil, a terpene $C_{10}H_{16}$ (Hardy). Harnack and Meyer state that the formula for pilocarpine is $C_{11}H_{16}N_2O_2$, and that its effects resemble those of nicotine; also that jaborandi yields another alkaloid, *jaborine*, $C_{22}H_{32}N_4O_4$, which is allied to atropine in its effects. Pilocarpine nitrate, $C_{11}H_{16}N_2O_2$, HNO_3, (*Pilocarpinæ Nitras*, B.P.) is official. Pilocarpine has a faintly bitter taste, and is soluble in water and in alcohol (90 per cent.). Concentrated sulphuric acid forms with it a yellowish solution which, on the addition of potassium bichromate, gradually acquires an emerald-green colour. It leaves no ash when burned with free access of air. It causes contraction of the pupil of the eye. Merck states that a third alkaloid, *pilocarpidine*, $C_{10}H_{14}N_2O_2$, is present in jaborandi. Harnack thinks that pilocarpine is probably a methyl derivative of pilocarpidine; Merck has shown that the base to which Harnack gave the name pilocarpidine does not yield pilocarpine by methylisation, and that the isomer obtained by this operation differs from pilocarpine in being insoluble in water. Merck, confirmed by Hardy and Calmels, states that jaborine is derived from pilocarpine by natural oxidation, while pilocarpidine by oxidation yields *jaboridine*, $C_{10}H_{12}N_2O_3$. The latter chemists have obtained pilocarpine artificially, β-pyridyl-α-lactic acid being converted into pilocarpidine, and this into pilocarpine.

Piperine, $C_{17}H_{19}NO_3$, is a feebly basic alkaloid occurring in *White*, *Black* (*Piper Nigrum*, B.P.), and *Long Pepper* (*Chavica officinarum*, Mign.), and in *Cubeb Pepper* (*Cubebæ Fructus*, B.P.), associated with volatile oil and resin; to these substances the odour, flavour, and acridity are due. Piperine is obtained on boiling white pepper with alcohol, and evaporating the liquid with solution of caustic potash, which retains the resin. Recrystallized from alcohol, piperine forms colourless prisms fusible at 212° F. (100° C.). With acids and certain metallic compounds it forms salts, and distilled with concentrated alkali yields *piperidine*, $C_5H_{11}N$, an alkaloid of strongly marked properties, and *piperic acid*, $C_{12}H_{10}O_4$. Piperidine is interesting as being one of the alkaloids that has been obtained artificially by Ladenburg. It is hexa-hydro-pyridine, and is obtained by the hydrogenization of pyridine (by the action of sodium in presence of alcohol). Johnstone finds it in long pepper and in ordinary pepper, more especially in the husk. According to Buchheim the amorphous resin of the peppers is similar in constitution to piperine, alkalies breaking it up into piperidine and *chavicic acid*. *Pyrethrin* is also said to decompose in an analogous manner. The piperine of cubeb pepper is not to be confounded with *cubebin*, a neutral constituent and having the formula $C_{10}H_{10}O_3$. Piperidine acid tartrate, a crystalline salt easily soluble in water, is a good solvent for uric acid.

Sanguinarine is the alkaloid of *Blood Root* (*Sanguinaria Canadensis*). Its salts are red. König and Tietz find five distinct alkaloids in the root of sanguinaria, viz., *chelerythrine*, $C_{21}H_{17}NO_4$; *sanguinarine*, $C_{20}H_{15}NO_4$; *α-homochelidonine*, $C_{21}H_{21}NO_5$; *β-homochelidonine*, $C_{21}H_{21}NO_5$; and *protopine*, $C_{20}H_{17}NO_5$. Protopine was found in opium by Hesse. It also occurs in *Celandine* (*Chelidonium*, U.S.P.), and is identical with *macleyine* obtained by Eyckmann from *Macleya cordata*.

Scopolamine.—*See* **Hyoscine.**

Solanine.—This alkaloid exists in the Woody Nightshade, or Bitter-sweet (*Solanum dulcamara*). It occurs also in the shoots, and in minute amount in the skins, of the tubers of the Potato (*Solanum tuberosum*). This alkaloid is only slightly soluble in water, alcohol, or ether; nitric acid colours it yellow; sulphuric acid produces at first a yellow, then a violet, and finally a brown coloration. By the action of dilute acids it is easily converted into a sugar and *solanidine*. Geissler finds *dulcamarin*, $C_{22}H_{34}O_{10}$, a glucoside, to be the bitter constituent of *Solanum dulcamara*. Sulphuric acid and alcohol, or either selenic acid or sodium selenate and sulphuric acid, colours solanine or solanidine a dark red.

Sparteine, $C_{15}H_{26}N_2$, is a poisonous volatile alkaloid occurring in Broom-tops (*Scoparii Cacumina*, B.P.). Its discoverer, Stenhouse, considers that the diuretic principle of broom is *Scoparin*, $C_{20}H_{20}O_{10}$, a non-poisonous substance, sparingly soluble in cold water. Mills has obtained ethyl-sparteine, $C_{15}H_{25}C_2H_5N_2$, and diethyl-sparteine, $C_{15}H_{24}(C_2H_5)_2N_2$. Apparently sparteine contains two pyridine nuclei. *Sparteinæ Sulphas*, U.S.P., has the formula $C_{15}H_{26}N_2,H_2SO_4,4H_2O$.

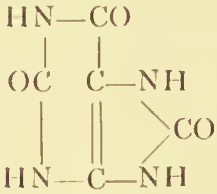
Stillingine.—Bichy states that this alkaloid is present in *Stillingia sylvatica* or *Queen's Root*.

TAXINE, $C_{37}H_{52}NO_{10}$? is an alkaloid occurring in the yew.

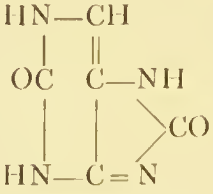
THEINE.—*See* CAFFEINE.

THEOBROMINE, $C_7H_8N_4O_2$, is an alkaloid occurring in *cocoa*, the seed of *Theobroma Cacao*, to the extent of 1 to 2 per cent. According to Schmidt, a little caffeine is present also. Theobromine is also present in Kola-nut (Heckel and Schlagdenhauffen). The caffeine in cacao, kola, and tea, is said to occur normally as a glucoside, which would explain why it is only partially extracted by chloroform from a mixture of either of these substances with lime.

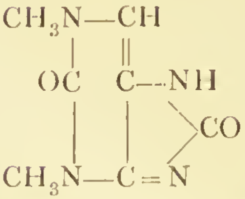
Relations between Caffeine and Theobromine.—Both caffeine and theobromine are methyl derivatives of xanthine, $C_5H_4N_4O_2$ (belonging to the uric acid group, uric acid having the formula $C_5H_4N_4O_3$). Caffeine, or trimethylxanthine has been obtained synthetically from uric acid by Fischer and Ach. Theobromine, or dimethylxanthine may be obtained from a silver derivative of xanthine by the action of methyl iodide; and caffeine (methyltheobromine) may be obtained by heating theobromine-silver with methyl iodide (Strecker). Theophyllin, isomeric with theobromine, was obtained by Kossel from tea extract.



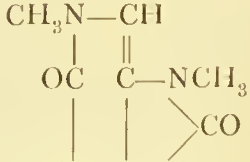
Uric acid



Xanthine



Theobromine or dimethylxanthine



Caffeine or trimethylxanthine

TRIGONELLINE, $C_7H_7NO_2$, H_2O.—Jahns states that this alkaloid, as well as one identical with choline, are present in the seeds of *fœnugreek* or *fenugreek* (*Trigonella Fœnum-græcum*) much used in veterinary medicine, and in some varieties of cattle food and curry powder.

TROPINE.—*See* ATROPINE.

TYLOPHORINE.—*See* EMETINE.

VASICINE, occurring as adhatodate, has been shown by Hooper to be the active principle of the leaves of *Adhatoda vasica*, or *Rus* (Hind.) or *Bakas* (Beng.) or *Vasaka* (Sanskrit), an official Indian expectorant (*Adhatoda*, B.P. Add. 1900).

VERATRINE, or VERATRIA, $C_{37}H_{53}NO_{11}$.—This alkaloid occurs in *Cevadilla*, the seeds of *Schœnocaulon officinale*, of A. Gray (termed *Asagræa officinalis* by Lindley), and *Veratrum officinale* by Schlecht. It is also said to occur in the leaves of *Sarracenia purpurea*. According to Weigelin, cevadilla contains two isomeric varieties of veratrine, the one soluble the other insoluble in water. He says there are also present *sabadilline* and *sabatrine*. The veratrine of trade contains the two latter alkaloids (Weigelin). A mere trace of veratrine brought into contact with the mucous membrane of the nose causes violent fits of sneezing. These alkaloids, and those from the different species of Veratrum, are evidently very closely allied. Wright and Luff, by the use of tartaric acid, a solvent less likely than the stronger acids to decompose alkaloids, extract from cevadilla, *veratrine*, $C_{37}H_{53}NO_{11}$; *cevadine*, $C_{32}H_{49}NO_{9}$; and *cevadilline*, $C_{34}H_{53}NO_{8}$. According to Merck, cevadilla contains two alkaloids, *sabadine*, $C_{29}H_{51}NO_{8}$, and *sabadinine*, $C_{27}H_{45}NO_{8}$.

The official process for the preparation of the alkaloid (*Veratrina*, B.P.) consists in exhausting the disintegrated cevadilla-seeds with alcohol (90 per cent.), recovering most of the alcohol by distillation, pouring the residue into water, by which much resin is precipitated, filtering, and precipitating the veratrine from the aqueous solution by addition of ammonia. It is purified by washing with water, solution in dilute hydrochloric acid, decolorization of the liquid by animal charcoal, reprecipitation by ammonia, washing and drying. Bosetti states that it is a mixture of crystalline cevadine, insoluble in water, with an amorphous isomeric soluble alkaloid, *veratridine*. According to Lissauer their physiological action is identical.

Unguentum Veratrinæ, B.P., contains 10 grains of the slightly impure alkaloid obtained as just described, rubbed with 40 grains of oleic acid, and mixed with about an ounce of lard.

NEW REACTIONS FOR THE DETECTION OF SOME ALKALOIDS (Brunner and Strzyzowski).*

	Chloral.	Bromal.	Paraldehyde.	Furfurol.	Ortho-nitro-phenylpropiolic acid.
	A crystal of chloral hydrate and 15 drops of sulphuric acid are heated with the substance.	Test applied in same way as in the case of chloral.	One drop of paraldehyde and 5 drops of sulphuric acid added to the substance.	The substance is mixed with 4 to 5 drops of a freshly prepared solution of furfurol (2 drops of furfurol and 10 c.c. of sulphuric acid).	The substance is mixed with 4 to 5 drops of a solution of 0·05 grm. of the above acid in 100 c.c. of sulphuric acid.
Morphine . . .	Grass-green; wine-red after the addition of water and caustic soda.	Same as with chloral hydrate.	Orange.	Brilliant red; olive-green on heating.	Violet on heating.
Codeine . . .	Grass-green.	Green; then blue.	Orange.	Red.	Violet on heating.
Apomorphine . .	Grass-green.	Greenish-blue.	Violet or red.	Red on heating; afterwards greenish.	Violet on heating.
Narcotine . . .	Greenish-yellow; afterwards red or violet. All the reagents give the same reaction, which is probably due to the sulphuric acid alone.				
Narceine . . .	Yellow; red; afterwards brown or reddish-brown (similar with all the reagents).				
Papaverine . .	Violet; decolorized on heating; afterwards rose.	Same as with chloral hydrate.	Reddish-yellow; then red.	Violet on heating; as with sulphuric acid alone.	Violet; reddish on heating.
Thebaine . . .	Coloured red by all the reagents, as by sulphuric acid alone.				
Quinine . . .	Does not exhibit any special colour indications.				
Strychnine . .	Bright-yellow. No other special reactions.				
Atropine . . .	Same behaviour as strychnine.				
Solanine . . .	Red-brown.	Red-brown or violet.	Orange or brick-red.	Ochre-coloured.	Yellow.
Colchicine . .	Does not exhibit any special colour indications.				
Veratrine . . .	Raspberry-red.	Raspberry-red.	Red-brown on heating.	Yellow; afterwards green.	As with sulphuric acid above.
Picrotoxin (glucoside) . .	Red.	Yellowish-red.	Yellow; red-brown on heating.	Yellow; passing into red-brown.	Reddish; afterwards olive-green.

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* *Schweizerische Wochenschrift für Chemie und Pharmacie*, 1898, p. 230.

1. TABLE TO AID IN THE IDENTIFICATION OF OFFICIAL ALKALOIDS, GLUCOSIDES, Etc.

Dissolve a grain or so in a few drops of water, or dilute hydrochloric acid, and add a drop of Mayer's solution (Potassium Mercuric Iodide), or of Potassium Bismuth Iodide.

A Precipitate indicates the presence of an Alkaloid.

No Precipitate indicates the absence of an Alkaloid. Search must then be made for glucosides, etc.

A. If the substance is colourless, or nearly so, then :—

To a small quantity on a porcelain plate add concentrated nitric acid.	Purple-red colour	Apomorphine	Confirm by ferric chloride and by sodium bicarbonate and chloroform.
	Blood-red ,,	Brucine	,, ,, stannous chloride.
	Orange-red ,,	Morphine	,, ,, ferric chloride and other tests.
	Yellow ,,	Codeine	,, ,, sulphuric acid and ferric chloride.
	Dirty-red ,,	Veratrine	*See* next section.
To another portion add concentrated sulphuric acid.	Red or brown on plate, deep-red if warmed in tube.	Veratrine	Confirm by heating with concentrated hydrochloric acid, which gives a reddish-purple colour.
	Blood-red colour	Salicin (glucoside).	Confirm by potassium bichromate and sulphuric acid.
If not found by preceding sections, heat a little in a dry tube.	Red vapours	Quinine	Confirm by thalleioquin reaction, etc.
		Quinidine	,, ,, ,, ,,
		Cinchonine	,, ,, ether test, etc.
		Cinchonidine	,, ,, ,, ,,

If not found by aid of the preceding sections, test specially as follows :—

1st. If an alkaloid—

Aconitine	Make a dilute solution and place a drop on the tongue—numbing and tingling.
Atropine	Alcoholic sol. added to alcoholic sol. of mercuric chloride and warmed—red precipitate. Homatropine gives a similar reaction; but *see* below.
Homatropine . . .	Add nitric acid, dry over water-bath, add alcoholic caustic potash—yellow coloration.
Caffeine	Murexid test.
Cocaine	Permanganate—purple precipitate. Boiled with caustic potash, then *slightly* acidified with hydrochloric acid and cooled—crystalline precipitate (of benzoic acid).
Physostigmine . . .	Warmed with caustic potash gives red colour which becomes bluish on evaporation to dryness; the residue dissolved in acid gives a dichroic solution.
Pilocarpine	*See* page 628.
Strychnine	Sulphuric acid and potassium bichromate.

2nd. If not an alkaloid—

Acetanilide	Heat with caustic potash and chloroform—unpleasant odour of phenyl-isonitrile or phenyl carbamine, C_6H_5NC.
Elaterin	With phenol and concentrated sulphuric acid—crimson colour, changing to scarlet.
Gluside (saccharin) .	Is extremely sweet.
Jalapin (purified Jalap Resin)	Insoluble in water or turpentine. Soluble in alkalies or alcohol, partly in ether. Acrid taste.
Naphthol	Soluble in boiling water, alcohol, ether, and chloroform. Add ammonia to hot saturated aqueous solution—blue fluorescence.
Phenacetin	Boil with hydrochloric acid, dilute, cool, filter, add bichromate—deep red.
Phenazone (antipyrin, analgesin)	To an aqueous solution add sodium nitrite and dilute sulphuric acid—deep green.
Picrotoxin	Compare a microscopic slide with one of picrotoxin similarly prepared.
Salol	Almost insoluble in water, soluble in alcohol, ether, and chloroform. Dissolve in alcohol; add ferric chloride—violet colour.
Santonin	Almost insoluble in water, but soluble in alkalies. A dilute solution of ferric chloride with an equal volume of concentrated sulphuric acid gives a red or violet colour.
Sulphonal	Heat with potassium cyanide (odour of mercaptan); add water, hydrochloric acid, and ferric chloride—deep red colour of ferric thiocyanate.

Note.—Acids are detected by the ordinary reactions carefully applied to small quantities of the substance.

Caution.—Any experiments in which contraction or dilatation of the pupil of the eye is involved should be made with extremely dilute solutions to begin with, say one drop of the solution of the substance under examination to one pint of water. If no effect is produced in an hour, it is easy then to make the experiment with a fluid of double this concentration, afterwards with one of twice the latter concentration, and so on. The chief dilating agents (mydriatics) are atropine, its isomers and homologues; and the chief contracting agents (myotics) are physostigmine and pilocarpine.

B. If the substance is coloured, seek the aid of the following memoranda :—

1st. If an alkaloid—

Beberine	Very bitter; caustic soda gives a yellow precipitate, soluble in ether.

2nd. If not an alkaloid—

Aloin	Very bitter; nitric acid gives a red colour (with socaloin brownish). Dissolved in concentrated sulphuric acid, with addition of a few drops of nitric acid, and diluted with water, it gives an orange or red colour, which is changed to deep claret on addition of ammonia in excess.
Chrysarobin	Scarcely soluble in water, soluble in alkalies with fine red colour. Concentrated sulphuric acid gives red-brown colour.
Jalap Resin	*See* above (may be almost white).
Podophyllin	Soluble in alcohol and precipitated by water. Soluble in ammonia and precipitated by acids. Taste slightly bitter.
Santonin	*See* above (white when fresh, but yellow after exposure to light).

[*To face page* 632.]

2. TABLE FOR THE QUALITATIVE A

<table>
<tr><td colspan="4">ALKALOIDS. { Quinine. Quinidine. Beberine. Cinchonine. Cinchonidine. Strychnine.</td><td></td></tr>
<tr><td colspan="4">Dissolve a portion in water, and add ammonia cautiously. Precipitate = alkaloids (except strychnine) and sometimes ferric hydroxide. Agitate the mixture with a little ether and separate, by means of a pipette, the ethereal solution, aqueous solution, and insoluble precipitate.</td><td>I</td></tr>
<tr><td colspan="2">Ethereal Solution.</td><td>Aqueous Solution.</td><td>Insoluble Precipitate.</td><td>A</td></tr>
<tr><td colspan="2">May contain quinine, quinidine, or beberine. To solution in a test-tube add water very slightly acidulated with acetic acid, boil, burning off the ether. To a portion of the acetic solution add chlorine or bromine water, then ammonia.</td><td rowspan="3">May contain strychnine. Agitate with chloroform and separate the chloroformic solution. Evaporate the chloroformic solution and moisten residue with concentrated sulphuric acid. Draw across the acid film a small crystal of potassium bichromate, moistened with sulphuric acid, when a transient play of colours—violet to red = <i>strychnine</i>. No colours = no strychnine.
In case of doubt add ammonia to original solution, agitate with chloroform, and proceed as before.</td><td rowspan="3">Is cinchonine, cinchonidine, or ferric hydroxide (red).
Saturate a drop or two of acetic acid in a little water with the precipitate, and to part of the solution add sodium tartrate: a precipitate occurs in the case of <i>cinchonidine</i>, and no precipitate in that of <i>cinchonine</i>.</td><td>Py phero of th origin potas nitric</td></tr>
<tr><td>Green Colour (thalleioquin).</td><td>No Green Colour.</td><td rowspan="2">Whi tate nitric <i>pyrop</i> <i>acid.</i></td></tr>
<tr><td>Solution is fluorescent, and contains either quinine or quinidine. Concentrate the remainder of the solution and divide into two parts. To one add potassium iodide and to the other add ammonium oxalate.
The former precipitates <i>quinidine</i>, not quinine. The latter precipitates <i>quinine</i> not quinidine.
For other methods <i>see</i> pages 605 and 606.</td><td>To a portion of the acetic solution add caustic potash, a yellowish white precipitate = <i>beberine</i>.</td></tr>
</table>

[*Table* 2. *To face p.* 632.]

IS OF ORDINARY SCALE COMPOUNDS.

'HOSPHORIC.
?HOSPHOROUS (generally converted into pyrophosphoric).
URIC.
OCHLORIC (as a contamination).
.RIC.
:.

INORGANIC BASES.
- AMMONIUM (often as a contamination).
- FERRIC SALT.
- POTASSIUM.
- SODIUM.

all quantity. Heat the ash with nitric acid, and add an olution of ammonium molybdate in nitric acid, and boil.

PRECIPITATE.

›ric or hypophos- Precipitate some s solution of the nce with caustic neutralize with add silver nitrate.

White to black precipitate soluble in nitric acid = *hypophosphorous acid.*

NO YELLOW PRECIPITATE.

Precipitate some of the aqueous solution of the original substance with caustic potash, filter, and add to a portion of the filtrate a slight excess of nitric acid; divide into two parts. To one add barium chloride (ppt. = *sulphuric acid*). To the other add silver nitrate (ppt. = *hydrochloric acid*). Neutralize another portion of the alkaline filtrate with nitric acid and add silver nitrate.

PRECIPITATE GREY TO BLACK.

Add very little ammonia (not sufficient to dissolve the whole precipitate) and warm. A silver mirror = *tartaric acid.*

Calcium chloride and lime-water ppt. a neutral solution (if concentrated) in the cold, the precipitate redissolving on boiling.

PRECIPITATE WHITE.

Citric acid gives imperfect or no silver mirror.

Calcium chloride and lime-water do not precipitate citric acid in the cold, but upon boiling (if solution be sufficiently concentrated) precipitation occurs.

Confirm tartaric or citric acid.—To slightly acidified caustic potash filtrate add ammonia in slight excess and considerable quantity of chlorides of ammonium and calcium. *Tartrate* is precipitated completely in the cold after agitation and subsequent standing for about ten minutes. To the solution (or filtrate, if tartrate is present) add three volumes of alcohol (90 per cent.); *citrate* is precipitated. If sulphates have been found, the alcohol may precipitate calcium sulphate, which must not be mistaken for calcium citrate.

Ammonium.—Boil aqueous solution with caustic potash and test vapour for ammonia. Filter and dissolve precipitate in hydrochloric acid, and test the solution for *iron* by ferrocyanide, thiocyanate, etc.

Potassium and sodium.—Ignite a small quantity, and moisten the residue with water. Test moistened residue with litmus-paper. If alkaline, examine for potassium and sodium by the colour imparted to the Bunsen flame, and for potassium by the bismuth thiosulphate test.

QUESTIONS AND EXERCISES

How is aconitine prepared?—Give the strengths of the official preparations of atropine.—Describe the properties of atropine.—What is the active principle of stramonium?—Mention official preparations containing cocaine and beberine.—Give the characters of beberine.—In what does nectandrine differ from beberine?—Mention the characteristics of conine.—What are the active principles of ipecacuanha?—Name the alkaloid of tobacco.—Give the properties of the alkaloid of Calabar bean.—What are the sources of piperine?—Whence is caffeine obtained; what is its relation to theobromine?—Describe the preparation of veratrine.—State the properties of veratrine.

Here the student is recommended to qualitatively analyse unnamed specimens (previously selected for him) of the free and ombined organic substances included in the appended Tables 1 *nd* 2.

SOME IMPORTANT PROXIMATE CONSTITUENTS OF ANIMAL AND VEGETABLE ORGANISMS

Proteid Principles, or Albumenoids

Albumen.—Agitate, thoroughly, some white of egg (*Albu-en*, B.P.) with water, and strain off the liquid from the occulent membranous insoluble matter. One part of white f egg to 4 parts of water forms the "Solution of Albu-en," B.P.

Test.—Heat a portion of this solution of albumen to the oiling-point; the albumen becomes insoluble, separating in ots or coagula of characteristic appearance.

Other Reactions.—Add to small quantities of aqueous soluon of albumen solutions of mercuric chloride, silver nitrate, ipric sulphate, lead acetate, alum, stannic chloride, or any the salts of the heavy metals; the various salts not only agulate, but form insoluble compounds with, albumen. ence the value of an egg as a temporary antidote in cases of isoning by many metallic salts, its administration retarding the absorption of the poison until the stomach-pump or other means can be applied. Sulphuric, nitric, and hydrochloric acids coagulate albumen; the coagulum is slowly re-dissolved by aid of heat, a brown, yellow, or purplish-red colour being produced. Neither acetic, tartaric, nor organic acids generally, except picric and gallotannic, coagulate albumen. Alkalies prevent the precipitation of albumen, and hence, in testing for albumen when only a trace is suspected to be present, it is well to make the fluid *very faintly* acid with acetic acid. Excess of acid acts like alkali in preventing coagulation but not so powerfully; in one case the absence of coagulation is due to the formation of acid albumen and in the other to the formation of alkali albumen, both of which are products formed by the partial disintegration of the proteid molecule and combination of the portions of the disintegrated molecule with the alkali or acid.

The products so formed are soluble even on boiling and hence no coagulation occurs when *dilute* solutions of albumen are boiled in presence of excess of alkali or acid.

Yolk or *Yelk of Egg* contains 16 per cent. of proteid, and 32 per cent. of fatty matter. The greater part of the proteid is in combination either with nucleins, among which the iron-containing nucleo-proteid is of importance as a hæmoglobin producer; or with the phosphorized fats or lecithins, forming lecith-albumens or vitellins.

Albumen is met with in large quantity in the serum of blood, in smaller quantity in chyle and lymph, and in the vascular tissues generally. It is not a normal constituent of saliva, gastric juice, bile, or mucus, but may occur during inflammation. It is found in the urine and fæces only in certain diseased states of the system.

Albumen is a highly complex substance, and its formula and chemical constitution are at present unknown. Egg albumen has been shown by direct determinations of osmotic pressure to possess in solution a molecular weight of about 10,000, while serum albumen has a molecular weight of about 50,000. Solutions of albumen, probably on account of the large size of the molecule, do not diffuse through parchment paper and in this way may be dialysed from admixed crystalloids (*i.e.*, substances which separate from solution in crystalline form, as contrasted with *colloids*, or glue-like substances, which do not crystallize). This method of separation is often of practical importance in medico-legal analyses.

Egg-albumen (and, to some extent, blood-albumen) is largely used by calico-printers as a vehicle for colours, serving also, when dry, as a glaze. Curriers prize egg-oil for softening leather.

Fibrin, Casein, Legumin.

Fibrin is the substance formed when blood or lymph undergoes coagulation. It is produced in the blood in the process of coagulation from a very unstable compound termed *fibrinogen.* The fibrinogen is attacked after the blood is shed by a ferment which is formed from the disintegrating white corpuscles. These corpuscles yield a substance which combines with the calcium salts present in the fluid, to form a soluble ferment termed *thrombosin* or fibrin ferment. The thrombosin then acts upon the fibrinogen and converts it into insoluble fibrin in the form of long threads of substance which bind the red corpuscles into a solid clot. Fibrin may be obtained by whipping fresh blood with a bundle of twigs, separating the adherent fibres, and washing in water until free from red corpuscles. It may best be kept in equal parts of glycerin and water.

Average Composition of Blood.—In human blood the moist corpuscles and *plasma* make up nearly equal parts; thus A. Schmidt found in blood obtained by venesection, 52·1 parts of plasma and 47·9 parts of corpuscles. The plasma contains approximately 8 to 10 per cent. of coagulable proteids of which only about 0·2 to 0·4 per cent. is fibrinogen, 3 to 4 per cent. globulin, and 5 to 6 per cent. albumen. In addition there are about 0·6 per cent. of other organic constituents, including about 0·15 per cent. of glucose which forms the circulating carbohydrate of the body. The inorganic salts amount to about 0·8 per cent., the salt present in largest amount (0·6 per cent.) is sodium chloride.

Caseinogen occurs in Cow's Milk to the extent of about 4 per cent., dissolved by a trace of salt of an alkali-metal. Its solution does not spontaneously coagulate, like that of fibrin, nor by heat like albumen; but acids cause its precipitation from milk in the form of a curd containing the fat globules (butter) previously suspended in the milk, a clear yellow liquid (or whey) remaining. Caseinogen, like fibrinogen, is capable of being changed into an insoluble form by the action of an unorganized ferment or enzyme. The insoluble form is termed *casein*, and is produced in the manufacture of cheese. The ferment is called *rennin*, or *chymosin*, and is contained in rennet, which is an extract prepared commercially from the salted and dried mucous membrane of the fourth stomach of the calf, but it is also present in the gastric mucous membrane not only of all mammals, but in birds and fishes. Similar milk-coagulating enzymes are found in the pancreatic juice, and in the juices of the stems and leaves of many plants. As in the case of fibrinogen, calcium salts are necessary in order that coagulation may occur.

A rennet extract may be prepared by extracting the salted mucous membrane with ten times its volume of a 5 per cent. solution of sodium chloride (to which 1 part in 10,000 of boric acid may be added as a preservative) for about seven days at room temperature. The fluid should be stirred up occasionally. Such an extract will coagulate 10,000 to 50,000 times its own volume of fresh milk.

Average Composition of 1000 parts of Milk.

	Specific gravity.	Water	Solid constituents.	Casein and extractive.	Sugar.	Butter.	Salts.
Human .	1·030 to 1·034	870	130	27	60	40	3
Cow's .	1·030 to 1·035	877	123	40	46	30	7

Leeds put the average composition of human milk at 2 per cent. of proteids, 7 per cent. of milk sugar, 4 per cent. of fat, and 0·2 per cent. of ash.

Specific gravity alone, as taken by the form of hydrometer termed a *lactometer*, or even by more delicate means, is of little value as an indication of the richness of milk, the butter and the other solids exerting an influence in opposite directions. Good cow's milk affords from 10 to 12 per cent. by volume of cream, and 3 to 3½ per cent. of butter. The water of milk seldom varies more than from 87 to 88 per cent., and the solid constituents from 13 to 12. Indeed, excluding its butter, milk is curiously regular in composition. The non-fatty solids in the mixed milk of a herd or dairy of healthy cows is almost a constant quantity, namely, 9·3 per cent. A lower proportion of non-fatty solids in a sample of milk points to the addition of water. Thus, supposing that 100 grains of a specimen of milk, evaporated to dryness, and all butter extracted from the residue (previously disintegrated by help of 1 or 2 parts of dried gypsum, or the dried infusorial earth termed *Kieselguhr*) by means of ether, yielded a non-fatty residue of 7·44 grains, the specimen would probably be four-fifths milk and one-fifth water.* Occasionally, under exceptional circumstances, a sample of genuine milk may be somewhat poorer than that from a healthy herd, and therefore, for legal purposes, a standard of 8·5 per cent. by weight of non-fatty solids and 3 per cent. of butter-fat has now been adopted. Only in the rare cases of milk containing an unusually large proportion of butter-fat could any milk yielding less than 8·5 per cent. of non-fatty solids be regarded as genuine. And, again, no milk would be considered genuine, under this standard, if it yielded less than 3 per cent. of fat, not even in the rare case of its containing an unusually large proportion of real non-fatty milk-solids. Cows in bad condition might yield milk below these standards; but it could scarcely be considered to be normal, or better fitted for food than milk watered *after* leaving the cow. If, therefore, a sample of milk is to be regarded as genuine, the standard of 8·5 per cent. of non-fatty solids and 3 per cent. of fat cannot be regarded as too high.

When examined under the microscope, milk presents a characteristic field of minute highly refractive globules consisting of the suspended fatty matter, which yields on separation the cream, or, when the globules are broken by agitation and coalesced together as in churning, the butter. The fat is fluid at the normal temperature of the animal, and remains so until the milk is well agitated by churning or otherwise, or until the milk is frozen.

Legumin, or *vegetable casein*, is found in most leguminous seeds, and in sweet and bitter almonds. Peas contain about 25 per cent. of legumin.

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* Soxhlet determines fat by noting the specific gravity of an ethereal solution and then referring to tables showing percentage of fat in ethereal solutions of varying specific gravity.

Vegetable albumen is contained in many plant-juices, and is deposited in flocculi on heating such liquids. *Vegetable fibrin* is the name given by Liebig and Dumas to that portion of the gluten of wheat which is insoluble in alcohol and ether. *Spongine*, the organic matter of sponge, appears to be a proteid.

The various proteids differ somewhat in their elementary composition, and the results experimentally obtained by different competent observers even in the case of the same proteid (or, indeed, different analyses of the same proteid by the same observer) show enough variation to preclude the possibility of deducing empirical formulæ of any importance. The mean composition of proteids is, however, of some physiological importance, especially in the case of the nitrogen, a determination of which is often employed as a measure of total quantity of proteid, the total nitrogen being determined and this multiplied by 6·25, on the assumption that proteid on the average contains 16 per cent. of nitrogen. The following figures give the limits of variation in each of the elements found by different observers: carbon, 50 to 55 per cent.; hydrogen, 6·8 to 7·3 per cent.; nitrogen, 15 to 18 per cent.; oxygen, 21 to 24 per cent.; sulphur, 0·3 to 2 per cent.

Proteids are found also in combination with other organic groups such as carbohydrates, fats, phosphorized fats, and nucleins, so forming the vast class of compound proteids. Examples are hæmoglobin, the iron-containing colouring-matter of the blood; the nucleins which are proteids combined with carbohydrate-like reducing bodies; the nucleo-proteids which are abundant in cell nuclei and are compounds of organic nitrogenous substances (also containing phosphorus) called nucleins, with proteids; the lecith-albumens of egg-yolk already referred to; and casein which consists of proteid united to a phosphorus-containing radical.

Proteids are divided, according to their solubility in water and certain saline solutions into "albumens," or "albumins," "globulins," "albumoses," "peptones," etc. Some globulins and albumoses form most virulent poisons when injected *directly* into the blood stream; to this class of substances belong the poison of most venomous reptiles, and also certain vegetable poisons such as that contained in the seeds of *Abrus precatorius* (Jequerity). The albumoses of ordinary digestion are similarly poisonous when injected directly into the blood stream. All these poisonous substances are however, harmless when swallowed, being modified as they are absorbed from the intestines, and so converted into innocuous products.

Musk (*Moschus*, B.P.), "the dried secretion from the preputial follicles of *Moschus moschiferus*" (the Musk-deer), is a mixture of albumenoid, fatty, and other animal matters with a volatile odorous substance of unknown composition. "Artificial Musk," a synthetical compound having an odour resembling in quality and power that of natural musk, is trinitro-tertiary-butyl-toluene, $C_6HCH_3(NO_2)_3C(CH_3)_3$.

Gelatin-producing Substances

These nitrogenous substances, collectively known as *collagens* (glue-producing), differ, chemically, from the proteids in containing less carbon and sulphur and more nitrogen. They are contained in certain animal tissues, and on boiling with water yield a solution which has the remarkable property of solidifying to a jelly on cooling. In the process of boiling with water the collagen becomes hydrated and yields the gelatin or *glutin* which is hence called the hydrate of collagen. When gelatin is heated to 130° C. the reverse change occurs and collagen is re-formed. The tendons, ligaments, bones, skin, and serous membranes afford *gelatin* proper; the cartilages give *chondrin*, which differs from gelatin in composition and in being precipitated by vegetable acids, alum, and lead acetate, or subacetate. The purest source of gelatin is *isinglass* (B.P.), which is "the swimming-bladder or sound of various species of *Acipenser*, Linn., prepared, and cut into shreds." Small quantities are more easily disintegrated by a file than a knife. A recently prepared 2 per cent. aqueous solution forms the official "Solution of Isinglass," B.P. Gelatin (*Gelatinum*, B.P.) is officially defined as "the air-dried product of the action of boiling water on such animal tissues as skin, tendons, ligaments, and bones." *Glue* is an impure variety of gelatin, made from the trimmings of hides; *size* is glue of inferior tenacity, prepared from the parings of parchment and thin skins. "Among the varieties of gelatin derived from different tissues and from the same sources at different ages, much diversity exists as to the firmness and other characters of the solid formed on the cooling of the solutions. The differences between isinglass, size, and glue, in this respect, are familiarly known, and afford good examples of the varieties called weak and strong, or low and high gelatin. The differences are sometimes ascribed to the quantities of water combined in each case with the pure or anhydrous gelatin, part of which water seems to be intimately united with the gelatin; for no artificial addition of water to glue would give it the character of size, nor would any abstraction of water from isinglass or size convert it into the hard dry substance of glue. But such a change is effected in the gradual process of nutrition of the tissues; for, as a general rule, the tissues of an old animal yield a much firmer or stronger jelly than the corresponding parts of a young animal of the same species." (Kirke's Physiology.)

Gelatin is precipitated from aqueous solution by alcohol, mercuric chloride, chloroplatinic acid, tannic acid, and many of the usual proteid precipitants. Pure glutin or gelatin does not give Millon's reaction, that is, a white precipitate turning red on boiling, when treated with the mixed nitrates of mercury (Millon's reagent). This reaction is characteristic of all true proteids. The failure of this reaction in the case of gelatin indicates the absence of the tyrosin group from the gelatin molecule. Aqueous solution of gelatin is not, like that of albumen, coagulated by heat, nor is it precipitated by acids. By prolonged ebullition its gelatinizing power is destroyed.

PEPSIN

Pepsin (from πέπτω, *pepto,* I digest) is an enzyme existing in the gastric juice, which is secreted by the parietal cells of the gastric glands. The hydrochloric acid which accompanies it in the gastric secretion is formed by a different type of cell in the glands called the oxyntic cells. Pepsin is only active in an acid medium. The enzyme exists in the gland cells in a precursory form called *pepsinogen,* and the active pepsin is formed from this substance in the act of secretion.

Pepsin may be prepared in the following manner:—The cleansed mucous membrane of the stomach (of the hog, sheep, or calf, killed fasting) is scraped, and the scrapings are macerated in cold water for twelve hours; the pepsin in the strained liquid is then precipitated by lead acetate, the deposit washed once or twice by decantation, hydrogen sulphide passed through the mixture of the deposit with a little water to remove the whole of the lead, and the filtered liquid evaporated to dryness at a temperature not exceeding 105° F. (40·5° C.).

Pepsin (*Pepsinum*, B.P.) is officially described as "an enzyme obtained from the mucous lining of the fresh and healthy stomach of the pig, sheep, or calf. Tested as described in the following paragraph, it should dissolve 2500 times its weight of hard-boiled white of eggs."

It is obtained as "a light yellowish-brown or white powder, or pale-yellow translucent grains or scales, having a faint odour and a slightly saline taste free from any trace of putrescence, and liable to absorb moisture from the air. If 12·5 grammes of coagulated and firm white of fresh eggs, 125 cubic centimetres of acidulated water containing about 0·2 per cent. of hydrogen chloride (HCl), and 0·005 gramme of Pepsin, be digested together at 105° F. (40·5° C.) for six hours, and shaken frequently, the coagulated white of egg dissolves, leaving only a few small flakes, in an almost clear solution. The 'white of egg' should be prepared by boiling quite fresh eggs in water for fifteen minutes, then immersing them in cold water, and, as soon as sufficiently cool for handling, separating the whites, washing off any fragments of yolk or membrane with water, removing the water with a clean towel, then at once rubbing the whites through a sieve having twelve meshes to a centimetre, and using the product before it has lost moisture. For the 'acidulated water' mix the official Hydrochloric Acid with water in the proportion of 1 gramme to 156 cubic centimetres; this will give a solution containing about 0·2 per cent. of hydrogen chloride (HCl)."

The solvent action of pepsin and hydrochloric acid on proteids, leads to the formation of a complex mixture of acid albumen, albumoses, and peptones.

The albumoses are an intermediate stage in the conversion of coagulable proteid into peptones.

The product obtained by the artificial action of pepsin on various forms of proteid is known commercially as peptone.

Any form of proteid may be digested as above described with pepsin and hydrochloric acid, and various commercial peptones are so prepared from white of egg, minced meat, or blood fibrin. *Papain* is a proteolytic enzyme contained in the leaves of the papaw tree (*Carica papaya*) which has been utilized as an artificial digestive agent for proteids.

PANCREATIC FERMENTS

The pancreas (sweetbread) secretes a colourless fluid of alkaline reaction which contains enzymes acting respectively upon each of the three classes of foodstuffs, viz., a proteolytic enzyme called *trypsin* which converts proteids into albumoses and peptones in neutral or alkaline solution; an amylolytic ferment called *amylopsin* or *pancreatic diastase* which converts starches into dextrins and maltose; and a steatolytic or fat-splitting ferment called *steapsin* or *lipase* which hydrolyses fats into fatty acids and glycerin. Active extracts may be prepared by extracting the gland, which ought to be allowed to stand for some hours before extraction, with water faintly acidulated with acetic acid, with dilute alcohol (1 in 4), with equal parts of glycerin and water, or with lime water and glycerin.

In addition to the above-mentioned three enzymes, the pancreatic juice contains a fourth unnamed enzyme which has a coagulating action upon milk. The official pancreatic solution (*Liquor Pancreatis*, B.P.) is prepared by digesting the pancreas of the pig in diluted alcohol for seven days, and filtering.

Ferratin is an organic iron compound which has been isolated from pigs' liver, and is regarded as a normal constituent of the organs of the animal body, in the tissues of which it is stored up as a reserve material for the formation of blood.

BILE

The *gall* or *bile* of the ox (*Bos taurus*, Linn.), evaporated to one-fourth of its bulk and freed from mucus by agitating with twice its bulk of alcohol (90 per cent.), in which mucus is insoluble, filtering and evaporating, yields the official Purified Ox Bile (*Fel Bovinum Purificatum*, B.P.): the latter has the appearance of a yellowish-green soft resin, but is chiefly composed of two crystalline substances; the one is termed *sodium taurocholate*, $NaC_{26}H_{44}NO_7S$, the other is *sodium glycocholate*, $NaC_{26}H_{42}NO_6$. Both taurocholates and glycocholates readily undergo hydrolysis, the former yielding *cholic* or *cholalic acid*, $HC_{24}H_{39}O_5$, and *taurine*, $C_2H_7NO_3S$, the latter cholalic acid and *glycine*, *glycocoll*, or *amido-acetic acid*, $CH_2(NH_2)COOH$, a soluble crystalline substance having interesting physiological relations, for it is obtainable from gelatin (hence the name glycocoll or sugar of gelatin, from γλυκὺς, *glucūs*, sweet, and κόλλα, *kolla*, glue) and from hippuric acid.

Choline (χολή, *cholē*, bile), $C_5H_{15}NO_2$, is an alkaloid originally found in bile, where it is derived from decomposition of lecithin, but it occurs in the brain, etc., in cod-liver oil, and in plants—ergot, Indian hemp, ipecacuanha, etc.

Tests for Bile.—The presence of bile in a liquid such as urine, may be detected by the following test.

1. The inside of a porcelain capsule is wetted with the suspected liquid, one or two crystals of cane-sugar are added, and then a few drops of concentrated sulphuric acid.

The capsule is then gently warmed, care being taken not to char the contents, when a reddish coloration develops, rapidly changing to violet. This test is known as Pettenkofer's test, and depends upon the interaction between furfurol and the bile salts. The furfurol is produced by the action of the sulphuric acid on the cane-sugar.

2. Gmelin's test is given by the bile pigments, and is carried out by pouring the bile-containing fluid upon fuming nitric acid in a test-tube when coloured rings form at the junction of the two fluids, a green ring forming above, which lower down passes into blue and then into brown near the acid. Gmelin's test may also be made by wetting a piece of filter-paper with the suspected fluid and then adding a drop of fuming nitric acid which becomes surrounded by coloured rings as described above.

QUESTIONS AND EXERCISES

In what form is albumen familiar?—Name the chief tests for albumen.—Why is the administration of albumen useful in cases of poisoning?—Mention the points of difference between yolk and white of egg.—From what sources other than egg may albumen be obtained?—In what respects does fibrin differ from albumen?—Enumerate the chief constituents of blood.—How may fibrin be obtained from blood?—State the difference between casein, fibrin, and albumen.—What are the relations of cream, butter, curds and whey, and cheese, to milk?—Describe the microscopic appearance of blood and milk.—How much cream should be obtained from good milk?—What is the percentage of water in genuine milk?—Name the sources of vegetable albumen and vegetable casein.—Give the percentage of nitrogen in albumenoid substances.—Describe the chemical nature of musk.—In what lie the peculiarities of gelatin-producing substances?—To what extent do isinglass, glue, and size differ?—Whence is pepsin obtained, and how prepared?—Give the proximate constituents of bile.—What are the tests for bile?

COLOURING-MATTERS

The animal, vegetable, and mineral kingdoms abound in more or less brilliantly coloured natural substances which are frequently employed as dyes or pigments, while art has richly supplemented the number of such natural colouring-matters. In the following paragraphs some of the more useful of these materials are enumerated under their respective colours.

Yellow.—1. *Chrome yellow* occurs in more than a dozen shades (*see* Lead chromate). 2. *Fustic* or *yellow wood*, the wood of *Rhus Cotinus*, is coloured by *fisetin*, its leaves by *myricetin* (Perkin). 3. *Gamboge* (*see* p. 556). 4. *Ochre* is met with of many tints, under the names of *yellow ochre, gold yellow, gold earth* or *ochre, yellow sienna, Chinese yellow.* It is chiefly a mixture of iron oxyhydroxides with alumina and lime. It has been used from the earliest times. 5. *Orpiment* and *King's yellow* are arsenium sulphides. 6. *Persian berries*, or *Avignon grains*, contain a yellow principle termed *rhamnin* and other crystalline bodies; they are the product of two or three species of *Rhamnus.* 7. *Purree, piuri* or *Indian yellow*, is said to owe its colour to a magnesium compound of *euxanthin*, $C_{19}H_{18}O_{11}$. 8. *Quercitron* is the bark of *Quercus tinctoria:* it contains the yellow glucoside, *quercitrin*, $C_{21}H_{22}O_{12}$. 9. *Rhubarb* (*see* Chrysophanic acid). 10. *Saffron* (*Crocus*, B.P.), the dried stigma and part of the style of *Crocus sativus*, yields *polychroite* or *crocin*, an orange-red glucoside. Kayser gives the formula of crocin as $C_{44}H_{70}O_{28}$, and states that by interaction with water ($7H_2O$) it yields *crocetin*, $C_{34}H_{46}O_9$, and glucose ($9C_6H_{12}O_6$). Any admixture of calcium carbonate, barium or calcium sulphate, or similar powder, with saffron, is readily detected by placing a small sample in a glass of warm water and stirring, when insoluble powder is deposited. "Incinerated with free access of air, dried saffron does not deflagrate, and yields about 7 per cent. of ash" (B.P.). 11. *Turmeric,* the rhizome of *Curcuma longa,* owes its yellow colour to *curcumin,* a substance which crystallizes from alcohol in prisms. Jackson and Menke state that curcumin is an acid, and that its formula is $H_2C_{14}H_{12}O_4$. Apparently two yellow pigments are present. The colouring-matters of turmeric are readily dissolved by chloroform, while those of saffron, mustard, or the best East-Indian rhubarb are not. On this fact methods of detecting turmeric in those substances have been founded. 12. *Weld* (*Reseda luteola*) contains a durable yellow matter termed *luteolin* ($C_{20}H_{14}O_8$). 13. *Picric* or *carbazotic acid* (p. 504) is a very powerful yellow dye. 14. Dried and powdered carrots yield to carbon bisulphide a yellow colouring-matter, "carrotin," which is obtained on evaporating the solvent. It is said to be used in colouring butter.

Red.—1. *Alkanet,* the root of *Alkanna tinctoria,* Tausch, *Anchusa tinctoria,* Desf., yields *anchusin* or *alkannin,* $C_{15}H_{14}O_4$, a resinoid substance soluble in oils and fat. 2. *Annatto, arnatto,* or *arnotto,* a paste prepared by evaporating a strained aqueous extract of the seeds of *Bixa Orellana,* contains *bixin,* $C_{28}H_{34}O_5$, an orange-red, and *orellin,* a yellow, principle. 3. *Brazil-wood* (*Cæsalpinia Brasiliensis*) furnishes *brezilin,* $C_{16}H_{14}O_5$, the basis of several lakes; *sappan-wood* (*Sappan,* B.P. Add. 1900, the heartwood of *Cæsalpinia Sappan*) contains either *brezilin* or a closely allied substance, *sappanin; Camwood,* from *Baphia nitida,* contains a similar substance, perhaps *santalin.* 4. *Cinnabar,* Chinese red, Vermilion, or Paris red, is mercuric sulphide. It is a very ancient red pigment. 5. *Chrome-red* is a lead oxychromate. 6. *Cochineal* (*see* p. 369). 7. *Madder,* the root of *Rubia tinctoria,* powdered and treated with sulphuric acid and acidulated water to effect the removal of earthy and other inert matters, furnishes a residual powder termed *garancin.* Garancin yields to pure water *alizarin,* $C_{14}H_8O_4$, the red, neutral, crystallizable colouring-matter of madder. Alizarin does not exist ready formed in the plant, but is derived, by fermentation, from a glucoside, termed *rubianic acid.* Alizarin is now largely produced artificially from *anthracene,* one of the solid constituents of coal-tar (*see* p. 475). 8. *Mulberry-juice* contains a violet-red colouring-matter which has not been chemically examined. 9. *Red lead* (*see* p. 250). This, and the following red ochre, are very ancient red colouring-matters. 10. *Red iron oxide*, of shades varying from light to brown-red, is found native. The common names of it are Armenian bole, Berlin red, colcothar, English red, red ochre, burnt ochre, red earth, terra di sienna, mineral purple, stone-red, and Indian red. 11. *Red sanders-wood* or *Red sandal-wood* or *barwood* (*Pterocarpi Lignum*, B.P.), the billets and chips of *Pterocarpus santalinus*, owes its colour to *santalin*, $C_{16}H_{14}O_3$, a crystalline substance possessing an acid character. Crystalline *pterocarpin*, $C_{10}H_8O_3$, and *homopterocarpin*, $C_{12}H_{12}O_3$, are also present (Cazeneuve). 12. *Red-Poppy Petals* (*Rhœados Petala*, B.P.), from *Papaver Rhœas*, contain a red colouring principle which has not yet been isolated in a state of purity. The author has sought for morphine in large quantities of the petals, but could not find a trace of that alkaloid. 13. *Red-Rose Petals* (*Rosæ Gallicæ Petala*, B.P.), and those of the Cabbage-Rose, also yield a red substance which has not been analysed. 14. *Safflower*, *dyer's saffron*, or *bastard saffron*, the florets of *Carthamus tinctorius*, contains an unimportant yellow dye, and 5 per cent. of *carthamin*, $C_{14}H_{16}O_7$, an uncrystallizable red dye, the pigment of the old *pink saucers*. Carthamin seems to possess acid characters, and (like silicic acid and other substances) to be soluble in water for a certain time after liberation from its alkaline solution; for fabrics are dyed with safflower by immersion in a bath made of an infusion in dilute alkali neutralized by citric acid immediately before use, the carthamin probably penetrating the cells and vessels of the fibres in a soluble form, there becoming insoluble and imprisoned, and thus giving permanent colour to the wool, silk, or other material. Mixed with French chalk, carthamin is used as a cosmetic under the name of *vegetable rouge*—*carmine* being *animal rouge*, and *red iron oxide* the *mineral rouge*. 15. *Lac-dye* is a cheap form of cochineal, and is also yielded by the species of *Coccus* whose resinous excretion constitutes *lac* (*stick-lac*, *seed-lac*, or *shell-lac*, according to its condition as gathered off the twigs on which it is deposited, or as roughly separated from impurities in seed-like powder or lumps, or as melted and squeezed through bags into shell-like pieces). 16. *Logwood* (*Hæmatoxyli Lignum*, B.P.) contains a yellow substance, *hæmatoxylin*, $C_{16}H_{14}O_6,H_2O$ (or $3H_2O$), to which any medicinal usefulness of the wood is perhaps due, and which, under the influence of air and alkali or ferments, assumes a very intense red colour—*hæmateïn.* Under the joint influence of ammonia and air hæmatoxylin yields greenish-violet iridescent scales of this *hæmateïn,* $C_{16}H_{12}O_6,3H_2O$. 17. *Red enamel* colours, for glass-staining and ceramic operations, are produced either by cuprous silicate or purple of Cassius (p. 221).

Blue.—1. *Cobalt oxide* precipitated in combination or admixture with alumina or calcium phosphate forms *Thénard's blue, cobalt-blue, Hoffner's blue,* and *cobaltic ultramarine.* 2. *Smalt, Saxony blue,* or *King's blue* is rough cobalt glass in fine powder (p. 152). 3. *Copper-blue, mountain-blue,* and *English* or *Hambro' blue* are chiefly copper oxycarbonates. 4. *Indigo,* B.P., $C_{16}H_{10}N_2O_2$, is a blue colouring-matter deposited when infusion of various species of *Indigofera* is exposed to air and slight warmth. Under these circumstances, *indican,* a yellow, transparent, amorphous substance, soluble in water, breaks up into indigo, which is insoluble and falls as a sediment, and a sugar termed *indiglucin.* The indigo is collected, drained, pressed, and dried. By the action of reducing agents indigo is converted into soluble colourless *indigogen, reduced indigo,* or *indigo white:* 1 part of powdered indigo, 2 of ferrous sulphate, 3 of calcium hydroxide, and 200 of water, shaken together and set aside in a well-closed bottle, yield this *colourless indigo,* $C_{16}H_{12}N_2O_2$. Linen or cotton yarn, or calico, dipped into such a solution and exposed to air, becomes blue, deposition of insoluble indigo-blue occurring within the cells and vessels of the fibre. This operation is readily performed on a small scale, and forms an illustration of a characteristic feature of the art of dyeing—namely, the introduction of soluble colouring-matter into a fabric by permeation of the walls of its cellular and vascular tissue, and the imprisonment of that colouring-matter within the cells and vessels by conversion into a solid and insoluble form (*see* also p. 159). Pure indigo, or *indigotin,* may be obtained in beautiful needles by spreading a paste of indigo and plaster of Paris on a tin plate, and when quite dry placing a lamp underneath, moving the latter from place to place as the indigo sublimes and condenses on the surface of the plaster. It may also be obtained in crystals by gently boiling finely powdered indigo with aniline, filtering while hot, and setting aside; these crystals may be washed with alcohol. Hot paraffin may be employed instead of aniline. Indigo may be produced artificially. Toluene, from coal-tar, was, by Perkin's process, converted into cinnamic acid, this into a nitro-derivative, and this again into orthonitrophenylpropiolic acid. From the latter, alkali and grape sugar deposited crystalline indigo (Baeyer). Other methods have since been devised. 5. *Litmus, lichen-blue, turnsole, orchil* or *archil*, and *cudbear*, are products of the action of air and alkalies on certain colourless principles, as *orcin*, $C_6H_3(OH)_2CH_3$, derived from different species of lichen—*Roccella, Variolaria*, and *Lecanora*. 6. *Prussian blue* (p. 181) and *Turnbull's blue* (p. 180) are met with under the names of *Erlangen, Louisa, Saxon, Paris*, or *Berlin blue*. 7. *Ultramarine*, a very old blue pigment, formerly obtained from the rare mineral, *lapis lazuli*, is now cheaply made on a large scale by roasting a mixture of fine white clay, sodium carbonate, sulphur, and charcoal or rosin. Its constitution is not well made out. Acids decompose it, hydrogen sulphide escaping.

PURPLE.—*See* MUREXID, p. 397.

GREEN.—1. *Cupro-arsenical* green pigments (p. 203). Most of the ancient greens contain copper carbonate. The original *emerald green* was a hydrous chromium oxide, but cupric aceto-arsenite is now sold under this name. 2. *Chlorophyll, leaf-green*, or *chromule*, is the substance to which the leaves of plants owe their green colour. It is resinoid, soluble in alcohol and ether, insoluble in water, and, on decomposition, yields a yellow and a blue substance (the phyllocyanin and phylloxanthin of Frémy and of Schunck). Recent researches tend to show that the chlorophyll obtained from different plants varies in composition. Chlorophyll would probably well repay extended investigation. 3. *Sap-green, buckthorn-, vegetable-*, or *bladder-green*, known also as *Chinese green*, or *lokas*, is obtained by evaporating to dryness a mixture of lime and the juice of the berries of buckthorn (*Rhamnus catharticus*). It is soluble in water, slightly soluble in alcohol, and insoluble in ether and oils. 4. *Green ultramarine* is made by a process similar to that for blue ultramarine. 5. Mixtures of blue and yellow pigments and dyes are common sources of green colours. 6. Glass and earthenware are coloured green by chromic oxide and cupric oxide.

BROWN.—1. *Umber, sienna,* or *chestnut-brown* is found native. By the action of heat it is darkened in tint, and is then known as *burnt umber.* It is a mixture of ferric oxide, silica, and alumina. 2. *Sepia* is a dried fluid from the ink-bag of cuttle-fishes (*Sepiadæ*); by its ejection into adjacent water the animal obtains opportunity of escape from enemies. 3. *Catechu* (p. 392) furnishes a brown colouring-matter.

BLACK.—1. *Blacklead* (p. 338), *bone-black* (p. 338) or *ivory-black,* and *lamp-black,* the latter a deposited soot from the incomplete combustion of rosin and tar, are varieties of carbon. 2. *Burnt sugar,* or *caramel* (p. 564). 3. *Indian ink* is usually a dried mixture of fine lamp-black and size or thin glue. 4. *Black writing ink* consists essentially of iron tannates and gallates suspended in water containing a little gum in solution. 5. *Printer's ink* is well-boiled linseed or other oil, mixed with good lamp-black, vermilion, or other pigment. 6. *Black dyes* are frequently of the same nature as ink. 7. The old "*pigmentum nigrum*" of black feathers, such as those of the common rook, of dark hair, and probably also of the skin of the negro, is, doubtless, the black substance which remains undissolved when black feathers are digested for some time in dilute sulphuric acid. It is said to have the formula $C_{18}H_{16}N_2O_8$ (Hodgkinson and Sorby).

WHITE PIGMENTS.—1. *Chalk* or *whiting* (pp. 117, 122). 2. *French chalk, steatite, talc,* or *soapstone,* is largely magnesium silicate. 3. *Heavy white* (p. 113). 4. *Pearl-white* (p. 258). 5. *Plaster of Paris* (p. 117). 6. *Starch* (p. 565). 7. *White lead* or Cremnitz white (p. 250). 8. *Zinc white* or *Chinese white* (p. 143). 9. "*Constant*" *white* is barium tungstate. 10. Toilet *flake white* is bismuth oxynitrate; artists' *flake white* is a form of dry white lead (p. 250). 11. Tin and zinc oxides and calcium phosphate are employed for giving a white opacity to glass.

ANILINE COLOURS. *Coal-tar colours.*—Within the past few years nearly every shade of colour seen in the animal and vegetable kingdoms has been successfully imitated by certain dyes and pigments primarily derived from a mineral, coal. Coal distilled for gas furnishes tar or gas-tar. Coal-tar contains some aniline; but especially it contains a liquid convertible into aniline, namely, benzene (C_6H_6), first discovered by Faraday in compressed oil-gas. From aniline, by oxidation, Runge obtained the violet-colour reaction, the substance producing which Perkin afterwards studied and isolated, and manufactured under the name of *mauve*. *Aniline-red* (*fuchsine*, *magenta*, or *rosaniline*), *aniline-yellow*, *aniline-green*, *aniline-blue*, and, in short, aniline-dyes, lakes, and pigments of the most varied hue are now common articles of trade. Their application has revolutionized the art of the dyer and colour-printer. Some of the coal-tar colours are not "aniline" colours, being derived from naphthalene, phthalic acid, phenol, etc.

QUESTIONS AND EXERCISES

Mention the chief yellow colouring-matters and describe their chemical nature.—What is annatto?—Name the colorific constituent of madder. Can it be made artificially?—State the source of litmus.—Distinguish between Prussian blue and Turnbull's blue; how are they manufactured?—How are they affected by acids?—Describe the chemical nature of the colouring principle of leaves.—By what agents is glass coloured green?—Whence is sepia obtained?—Describe the chemistry of black ink.—Write a few sentences on *aniline colours*.

QUALITATIVE ANALYSIS OF SUBSTANCES HAVING UNKNOWN PROPERTIES

Substances are presented to the analyst in one of the three forms in which all matter exists—namely, solid, liquid, or gaseous; and they may contain animal or vegetable as well as mineral matter.

The method of analysis in the case of *solid mineral bodies* has been described on pp. 406 to 416.

Solid animal or vegetable substances (or mixtures of these with mineral bodies) may be indefinite and beyond the grasp of chemistry, or definite and quite within the range of proximate qualitative organic analysis. The presence of such substances is indicated in the preliminary examination of a solid (pp. 407 to 410) by charring and other characters. If no charring occurs, and no volatile liquid is expelled by heat, the absence of such matter is indicated. But if organic matter is present, an endeavour is made to ascertain its precise character. The analyst's knowledge of the history of the substance, or the circumstances under which it comes into his hands, will probably afford a clue to its nature, and enable him to search directly for its proximate constituents. If no such information is at hand, the action of solvents may be employed, as likely to afford indication of the general, if not of the precise, nature of the substance. Water, alcohol, ether, chloroform, carbon bisulphide, each hot and cold, may in turn be agitated with the substance; each extract may then be filtered, a portion of the filtrate evaporated, at first partially, setting the product aside for the deposition of crystals, etc., and afterwards to dryness; and any deposit or residue may be examined with and without the aid of a microscope. Other portions of the filtrate may be treated with acids, alkalies, and solutions of such metallic salts as are commonly used as group-reagents for acid radicals (p. 404). The action of alkalies as well as acids, dilute and concentrated, hot and cold, may also be tried on the solid substance itself, and colours, odours, and, in short, any effect whatever, be duly noted. A portion of the substance should also be burnt in an open porcelain crucible until no carbon remains, and the ash, if any, be examined; its amount and nature may afford information leading to the identification of the substance.

The foregoing experiments having been carefully performed, and all results entered in the note-book, a little reflection will possibly lead to recognition, or may suggest further direct experiments or confirmatory tests, or will, at least, have pointed to the absence of a very large number of possible substances, and thus have restricted the area of inquiry to comparatively narrow limits. The success attainable in qualitative proximate organic analysis by the medical or pharmaceutical student will of course largely depend on the thoroughness with which the operator has prosecuted his study of practical chemistry generally; but it will be considerably affected also by the extent to which he has cultivated the art of observation, and the opportunities he has had of acquiring a knowledge of the appearance, uses, and common properties of definite chemical substances, and of articles of food, drink, and medicine. The most successful of several good analysts will be the one who has most common sense and most experience.

The pharmaceutical student, who has probably already had some years of experience in pharmacy, occupies an unusually favourable position for prosecuting the proximate analysis of organic and inorganic substances, or, at all events, of that large proportion of such substances met with in the domain of hygiene and pharmacy. Many substances he will identify at sight, or by aid of a lens, or after applying some simple physical or chemical test. Nor should he find much difficulty, after reaching the present point of practical study, in deciding whether the solid substance under examination belongs to the class of organic acids, organic salts of metallic radicals, alkaloids, alkaloidal salts, amylaceous matter, gums, saccharine substances, glucosides, albumenoid matters, fats, soaps, resins, colouring-matters, etc. For instance, the pharmaceutical student will find less difficulty than the general student in successfully analysing a substance occurring in "scales," because he has experience of the appearances of compounds commonly produced in that form, and because, even if the appearance is new to him, he knows what kind of substances most readily lend themselves to production in that form. While the general student is testing generally, and proceeding cautiously, or searching for general information in books of reference, the pharmaceutical or medical student has incinerated some of the material, noticed whether or not the ash is red (iron) and strongly alkaline (potassium), treated more of the material with an alkali (for ammonium), added excess of ammonia, and examined the precipitate (for cinchonine or quinine) or shaken up the alkaline liquid successively with ether and chloroform, and tested the residue of these decanted and evaporated solvents (quinine, beberine, strychnine), and examined the aqueous solution of the material, or one of the filtered alkaline liquids, in the usual way for acid radicals (citric, tartaric, sulphuric, hypophosphorous). Or he has modified his methods to include search for some "scale preparation" which his special knowledge tells him has been newly introduced to, or is rare in, pharmacy.

In the case of liquids, the solvents as well as the dissolved matters claim attention. A few drops are evaporated to dryness on platinum foil to ascertain if solid matter of any kind is present; the liquid is tested with red and blue litmus-paper, to ascertain if free alkalies, free acids, or neither are present; a few drops are heated in a test-tube and the odour of any vapour noticed, a piece of glass tubing bent to a right angle being, if necessary, adapted to the test-tube by means of a cork, and some of the distilled liquid collected and examined;

finally, the usual group-reagents for the several metallic and acid radicals are consecutively applied.

Proceeding in this way, the student who has already had some experience in pharmacy, will not be likely to overlook such solvents as water, acids, alkalies, alcohol, glycerin, ether, chloroform, benzene, fixed oils, and essential oils, or to miss the substances which these menstrua may hold in solution. He will probably also recognise such liquids as carbolic acid, formic acid, lactic acid, methyl alcohol, aldehyde, aniline, nitrobenzene. He must not, however, suppose that he will always be able to qualitatively analyse, say, a bottle of medicine so as to ascertain, with certainty, the substance from which it has been compounded ; for the various infusions, decoctions, tinctures, wines, syrups, liniments, confections, extracts, pill-masses, and powders contain vegetable matters many of which are at present almost beyond the reach of the analyst. Neither the highest skill in analysis nor the largest amount of experience concerning the odour, appearance, taste, and uses of drugs is sufficient for the certain detection of all these vegetable matters. Skill and experience combined, however, will do much ; and in most cases even so difficult a task as the one just mentioned may be accomplished with reasonable success. Obviously, qualitative analysis alone will not enable the operator to produce a mixture of substances similar to that analysed ; to this end recourse must be had to quantitative analysis, a subject treated subsequently.

Natural fluids, as "Milk" and "Urine," admit of special analytical treatment (*see* pp. 637 and 672).

Gas-analysis is a branch of chemical analysis, chiefly of a quantitative character, concerning which information must be sought in other treatises. The analysis of atmospheric air from various localities, coal-gas, and the gases produced in many technical operations or obtained in chemical researches, involves appliances and methods which are scarcely within the sphere of chemistry as applied to pharmacy or medicine. Beyond the recognition, therefore, of oxygen, hydrogen, nitrogen, chlorine, carbonic anhydride, sulphurous anhydride, nitrous gases, hydrogen sulphide, etc., the experimental consideration of the chemistry of gaseous substances may be omitted. Their study, however, should not be neglected, as existing theoretical conceptions regarding chemical substances are largely dependent on the observed physical behaviour and chemical relationships of gaseous compounds (*See* pp. 13 to 25; 36 to 39; 43 to 54.)

Spectrum Analysis.—It may be well to state here that the preliminary and final examinations of minute quantities of solid matter may, in certain cases, profitably include their exposure to a temperature at which they emit light, the flame being physically analysed by means of a spectroscope. The spectroscope consists essentially of a prism to decompose a ray of light into its constituent colours, with tubes and lenses to collect and transmit the ray or rays to the eye of the observer. The material to be examined is placed on the end of a platinum wire, which is then brought within the edge of the flame of a spirit-lamp or Bunsen burner; volatilization, attended usually in the case of a compound by decomposition, at once occurs, and in presence of certain substances the flame is tinged with a characteristic hue. When examined by means of the spectroscope the various coloured flames are found to be due in each case to rays of certain definite degrees of refrangibility, the latter being indicated by the arrangement of coloured "lines" (*i.e.*, images of the slit) present in the *spectrum* of the substance under examination. Sodium compounds, when examined in this way, give yellow light only, indicated by a double band of light in a position corresponding to a portion of the yellow part of an ordinary solar spectrum. The potassium spectrum is mainly composed of a red and violet band; lithium gives a crimson, and, at very high temperatures, a blue band, and so forth.

By passing white light through a coloured substance an "absorption spectrum" will be produced which is often characteristic, as in the case of blood or chlorophyll, solution of potassium permanganate, etc.

CHEMICAL TOXICOLOGY

In cases of criminal and accidental poisoning, the substances presented to the chemical analyst for examination are usually articles of food, medicines, or vomited matters; or the liver, kidneys, intestines, stomach and contents, removed in course of post-mortem examination. In these cases some special operations are necessary before the poison can be isolated in a state of sufficient purity for the application of the usual tests; for in most instances the large quantity of animal and vegetable, or, in one word, organic matter present, prevents or masks the characteristic reactions on which the tests are founded. These operations will now be described *; they form the chemical part of the subject of Toxicology (τοξικὸν, *toxicon*, poison, and λόγος, *logos*, discourse).

Substances occurring apparently as definite salts or unmixed with organic matter need no special treatment. They are analysed by the ordinary methods already given, attention being restricted to poisonous compounds.

EXAMINATION OF AN ORGANIC MIXTURE SUSPECTED TO CONTAIN:—MERCURY, ARSENIUM, ANTIMONY, LEAD, COPPER, CHROMIUM, OR ZINC; SULPHURIC, NITRIC, HYDROCHLORIC, OXALIC, OR HYDROCYANIC ACID; CAUSTIC ALKALIES; PHOSPHORUS; STRYCHNINE, MORPHINE, OR OTHER POISONOUS ALKALOID.

Preliminary Examination.

Odour, Appearance, etc.—Smell the mixture, with the view of ascertaining the presence or absence of any notable quantity of free hydrocyanic acid. Look carefully for any small solid particles, such as white arsenic, corrosive sublimate, or verdigris, and for any appearance which may be regarded as abnormal, any character unusual to the coffee, tea, beer, medicine, vomit, coats of stomach, kidney, liver, or other organ, tissue, or solid matter under examination.

Poisonous Quantity of Acid.—Add to a small portion some solution of sodium carbonate, with the view of ascertaining by strong effervescence the presence of any large, poisonous quantity of sulphuric, nitric, or hydrochloric acid (p. 658).

Poisonous Quantity of Alkali.—If so excessively alkaline as to require the addition of a very large quantity of acid before neutralization is effected, a noxious quantity of a corrosive or caustic alkali is present. Whether soda or potash, etc., is present is ascertained by the usual tests.

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* Materials for these experiments are readily obtained for educational purposes by dissolving the poison in infusions of tea or coffee, in porter or in water to which some starch mucilage or linseed meal, pieces of bread, potato, and fat have been added.

Special Instructions may induce the operator to suspect the presence of one particular poison. Direct examination for the latter may then be made, either at once, if the substance has an aqueous character, or when filtration or treatment with warm hydrochloric or acetic acid has afforded a more or less colourless liquid.

Fluids.—A vomit or the contents of a stomach, if set aside in a long narrow vessel (test-glass or ale-glass), or, better, exposed on a filter during a night, will often yield a more or less limpid portion at the bottom or top of the solid matter. This fluid (separated by a pipette or otherwise) will sometimes respond to tests without further preparation, and always requires less preparatory treatment than a semi-solid mixture. If none passes through a filter, a portion often collects as a lacuna in the upper part.

General Procedure.—If the preliminary examination does not indicate the method to be pursued, proceed as follows, treating a portion (not more than one-fourth) of the mixture for the poisonous metals, another for the acids, and a third for alkaloids, reserving the remainder for any special experiments which may suggest themselves.

Examination for Mercury, Arsenium, Antimony, Lead, Copper, Chromium, Zinc.

If a liquid, acidulate with hydrochloric acid and boil for a short time. If solid or semi-solid, cut up the matter into small pieces, add enough water to form a fluid mixture, stir in 10 to 20 per cent. of pure concentrated hydrochloric acid, and boil until, from partial aggregation and solution of the solid matter, filtration can be effected.

Heat a portion of the clear liquid with a thin piece of bright pure copper or copper gauze, about an inch long and a quarter of an inch broad, for about ten to twenty minutes; metallic *mercury, arsenium,* or *antimony* will be deposited on the copper, darkening it considerably in colour. Pour off the liquid from the copper, carefully rinse the latter with a little cold water, dry the piece of metal by holding it over or near a flame (using fingers, not tongs, or it may become sufficiently hot for loss of mercury or arsenium to occur by volatilization), introduce it into a narrow test-tube or piece of glass tubing closed at one end, and heat the bottom of the tube in a flame, holding it horizontally so that the upper part of the tube may be kept cool, and partially closing its mouth with the finger to prevent escape of vapour. Under these circumstances any *mercury* will volatilize from the copper and condense on the cool part of the tube in a ring or patch of white sublimate, readily aggregating into visible globules on being pressed by the side of a thin glass rod inserted into the tube; *arsenium* will volatilize from the copper, and, uniting with oxygen from the air in the tube, will condense on the cool part of the glass in a ring or patch of white sublimate of arsenic (grey or even darker if much arsenium as well as arsenic be present), not running into globules when rubbed, but occurring in small crystals, the characteristic octahedral form of which (*see* p. 196) is readily seen by aid of a good hand-lens or the low power of a microscope; *antimony* volatilizes from the copper if strongly heated, and, uniting with oxygen, immediately condenses as a slight white deposit of antimonious oxide close to the copper. (*See* p. 211.)

Confirmatory Tests.—1. Nothing short of the production of globules should be accepted as evidence of the presence of mercury. It will usually have existed as corrosive sublimate. 2. To confirm indications of the presence of arsenium, a portion of the acid liquid may be subjected to the hydrogen tests (pp. 197-200); or the tube containing the white crystalline arsenic may be broken, and the part on which the sublimate occurs boiled for some time in water, and the hydrogen sulphide, ammonio-silver nitrate, and ammonio-copper sulphate tests (pp. 203, 204) applied to the aqueous solution. 3. For antimony, a portion of the acid liquid must always be introduced into the hydrogen-apparatus with the usual precautions. (*See* p. 211.) 4. Any sulphur present may darken the copper, and such stained copper may subsequently yield a whitish sublimate of sulphur on the sides of the subliming tube; such appearances, therefore, are consistent with the entire absence of mercury, arsenium, and antimony.

Note.—Before finally concluding that arsenium is absent from a fluid, the latter should be warmed with a little sulphurous acid, and the ordinary tests then again applied; for arsenic acid and other arsenates are not readily affected by the usual reagents for arsenium.

For *lead* and *copper*, pass hydrogen sulphide through the clear acidulated liquid for some time, warming the liquid if no precipitate is produced, or diluting and partially neutralizing the acid by addition of ammonia if much acid has been added. Collect on a filter any black precipitate that may have formed; wash, dissolve in a few drops of aqua regia, dilute, and apply tests, such as ammonia for copper, sulphuric acid for lead, or any other of the ordinary reagents (pp. 231, 254).

Copper may often be at once detected in a small quantity of acidulated liquid by immersing the point of a penknife or a piece of bright iron wire—a deposit of copper, in its characteristic colour, quickly or slowly appearing, according to the amount present (p. 231).

Chromium and Zinc.—To the acid liquid through which hydrogen sulphide has been passed, add excess of ammonia (or to the original acid liquid add excess of ammonia, and then ammonium hydrosulphide); a precipitate falls which may contain alumina, phosphates, chromium, and zinc. (It is usually blackish, from the presence of ferrous sulphide.) Collect the precipitate on a filter, wash, dissolve in a little hydrochloric acid, add a few drops of nitric acid, boil, pour in excess of ammonia, filter, and test the filtrate with ammonium hydrosulphide; a white precipitate indicates zinc. A green precipitate would indicate chromium. Chromates should also be sought for (p. 185).

Examination for Mineral Acids, and for Oxalic and Hydrocyanic Acids.

To detect *hydrochloric, nitric,* or *sulphuric acid* in a liquid containing organic matter, dilute with water and apply to small portions the usual tests for each acid, disregarding indications of small quantities. (*See* pp. 287, 309, 333.)

Excessive acidity, copious evolution of carbonic anhydride on the addition of sodium carbonate, and very strongly marked reactions on the application of the usual reagents to small portions of the fluid presented for analysis, collectively form sufficient evidence of the occurrence of a poisonous amount of either of the three common mineral acids, but in important cases quantitative analyses should be made. Small quantities of the hydrochloric, nitric, and sulphuric radicals, occurring as metallic salts or acids, are common normal constituents of food ; hence the direction to disregard insignificant indications. If the fluid under examination be a vomit or the contents of a stomach, and an antidote has been administered, free acid may not be found, but, instead, a large amount of the corresponding salt.

For *oxalic acid,* filter or strain a portion of the liquid, if not already clear, and add solution of lead acetate so long as a precipitate is produced ; collect the precipitate, which in any case is only partly lead oxalate, on a filter, wash, transfer it to a test-tube or test-glass, add a little water, and pass hydrogen sulphide through the mixture for a short time ; any lead oxalate is thus converted into insoluble lead sulphide, while oxalic acid is set free in the solution. Filter, boil to get rid of hydrogen sulphide, and to the clear filtrate apply the usual tests for oxalic acid (*see* p. 345).

The contents of a stomach containing oxalic acid will often be of a dark-brown colour with a tinge of green (altered blood and mucus), and the viscid mixture generally, though slowly, affords some clear, limpid, almost colourless, liquid by filtration or on standing.

For *hydrocyanic acid,* the three chief tests may be applied at once to the liquid or semi-liquid organic mixture, whether it has an odour of hydrocyanic acid or not. First:— Half fill a small porcelain crucible with the material, add eight or ten drops of concentrated sulphuric acid, stir gently with a glass rod, and invert over the mouth of the crucible a watch-glass moistened with a small drop of solution of silver nitrate; a white film on the silver solution is probably silver cyanide, formed by the action of the gaseous hydrocyanic acid on the silver nitrate. Second:—Prepare a small quantity of the organic mixture as before, slightly moistening the centre of the watch-glass with solution of caustic potash; here, again, the heat generated by the action of the concentrated acid is sufficient to volatilize some of the hydrocyanic acid, which, interacting with the caustic potash, forms potassium cyanide. On removing the watch-glass and stirring into it successively solution of a ferrous salt, a ferric salt, and hydrochloric acid, flocks of Prussian blue are produced if hydrocyanic acid is present. Third:—Proceed as before, moistening the watch-glass with yellow ammonium hydrosulphide; after exposure to the hydrocyanic acid gas for five to ten minutes, add a drop of solution of ammonia, evaporate to dryness at a low temperature, then add a drop of hydrochloric acid and of solution of ferric chloride; a blood-red colour, due to ferric thiocyanate, is produced if cyanogen is present.

If the above reactions are not well marked, the organic mixture may be carefully and slowly distilled in a small retort, the neck of which passes into a bottle and dips beneath the surface of a little water at the bottom of the bottle; the reagents may then be applied to separate portions of the distillate.

The examination of organic mixtures for hydrocyanic acid must be made without delay, as the poison soon begins to decompose, and in a day or two may be destroyed.

Examination for Phosphorus.

A paste containing phosphorus is commonly employed for destroying vermin. In cases of poisoning, the phosphorus is generally in sufficient quantity to be recognised by its characteristic unpleasant smell. A stomach in which it occurs not infrequently exhibits slight luminosity if opened in a dark room. When the phosphorus is too small in quantity or too much diffused to afford this appearance, a portion of the material is placed in a flask, water acidulated with sulphuric acid added, a long wide glass tube fitted to the neck of the flask by a cork, and the mixture gently boiled. If phosphorus is present (even 1 part in 2,000,000, according to De Vrij) the top of the column of steam as it condenses in the tube will appear distinctly phosphorescent when viewed in a dark room. From its liability to oxidation, phosphorus cannot be detected after much exposure of an organic mixture to air.

Examination for Strychnine and Morphine.

Strychnine.—If solid or semi-solid, digest the matter with water and about 10 per cent. of hydrochloric acid till liquid, filter, evaporate to dryness on a water-bath. If the organic mixture is already liquid, it is simply acidulated with hydrochloric acid and evaporated to dryness. The acid residue is next treated with alcohol (90 per cent.) as long as anything is dissolved, the filtered tincture evaporated to dryness over the water-bath, and the residue digested in water and filtered. This slightly acid aqueous solution must now be rendered alkaline by the addition of ammonia, and well shaken in a closed bottle or long tube with about half an ounce of chloroform, and set aside till the chloroform has subsided. The chloroform (which contains the strychnine) is then removed by means of a pipette, the presence of any aqueous liquid being carefully avoided, and evaporated to dryness in a small basin over a water-bath, the residue moistened with concentrated sulphuric acid, and the basin kept over the water-bath for several hours. (It is highly important that the sulphuric acid used in this operation should be free from nitrous compounds. Test the acid, therefore, by adding powdered ferrous sulphate, which becomes pink if nitrous compounds are present. If these are found, the acid should be purified by strongly heating with ammonium sulphate, 70 or 80 grains to a pint.) The charred material is exhausted with water, filtered, excess of ammonia added, the filtrate shaken with about a quarter of an ounce of chloroform, the mixture set aside for the chloroform to separate, and the chloroform again removed. If on evaporating a small portion of this chloroform solution to dryness, adding a drop of sulphuric acid to the residue, and warming, any darkening of colour or charring takes place, the strychnine is not sufficiently pure for chemical detection; in that case the rest of the chloroform must be removed by evaporation, and the residue redigested in warm sulphuric acid for two or three hours. Dilution, neutralization of acid by addition of ammonia, and agitation with chloroform is again practised, and the residue of a small portion of the chloroform solution once more tested with sulphuric acid. If charring still occurs, the treatment must be repeated a third time. Finally, a part of the chloroform solution is taken up by a pipette and drop after drop evaporated on one spot of a porcelain crucible-lid until a fairly distinct dry residue is obtained. A drop of sulphuric acid is placed on the spot, another drop placed near, a minute fragment of potassium bichromate placed in the second drop, and, when the acid has become tinged with the chromate, one drop drawn across the other; the characteristic evanescent purple colour is then seen, if strychnine is present. Other tests (*see* p. 610) may be applied to similar spots.

This is Girdwood and Rogers's method for the detection of strychnine when mixed with organic matter. It is tedious but trustworthy, and, though apparently complicated, very simple in principle, thus—strychnine is soluble in acidulated water or alcohol, or in chloroform, readily removed from an alkaline liquid by agitation with chloroform, and not charred or otherwise attacked when heated to 212° F. (100° C.) with sulphuric acid: much of the organic matter of the food is insoluble in water; of that soluble in water, much is insoluble in alcohol; and of that soluble in both menstrua, all is charred and destroyed by warm sulphuric acid in a shorter or longer time. (*See* also Stas's general process, p. 664.)

Morphine and the Meconic Acid with which it is associated in Opium.—To the liquid or the semi-liquid mixture, warmed for some time with a small quantity of acetic acid, filtered, and concentrated if necessary, add solution of lead acetate until no further precipitate is produced. Filter and examine the *precipitate* for meconic acid, reserving the *filtrate* for the detection of morphine.

The precipitate.—Wash the *precipitate* (lead meconate, etc.) with water, place it in a test-tube or test-glass with a small quantity of water, pass hydrogen sulphide through the mixture for a short time, filter, slightly warm in a small basin, well stirring to promote removal of excess of the gas, and add a drop of neutral solution of ferric chloride; a red colour, due to the formation of ferric meconate, is produced if meconic acid is present. This colour is not destroyed on boiling the liquid after the addition of one drop of dilute hydrochloric acid, as is the case with ferric acetate, nor is it bleached by solution of corrosive sublimate, thus distinguishing it from ferric thiocyanate. It is discharged by hydrochloric acid.

The Filtrate.—The solution from which meconic acid has been removed by adding lead acetate is evaporated to a small bulk over a water-bath, excess of potassium carbonate added, and evaporation continued to dryness. The residue is then treated with alcohol, which dissolves the morphine. The alcoholic solution similarly evaporated may leave the morphine sufficiently pure for the application of the usual tests (*see* p. 598) to small portions of the residue. If no reaction is obtained, add a drop of sulphuric acid and a little water to the residue, and shake with ether, in which the morphine salt is insoluble. The treatment with ether may be repeated until nothing more is removed, the acid aqueous liquid saturated with potassium carbonate, the mixture evaporated to dryness, the residue digested in alcohol, filtered, and portions of the alcoholic liquid evaporated to obtain spots of morphine for the application of the ordinary tests.

If much organic matter is believed to remain in the filtrate after the lead acetate treatment, or if a considerable excess of lead acetate has been employed, the filtered liquid should be subjected to a current of hydrogen sulphide until no more lead sulphide is precipitated; the mixture should then be filtered, and the filtrate, with the washings from the lead sulphide, evaporated to a small bulk, excess of potassium carbonate added, the whole well mixed and agitated with twice or thrice its bulk of a mixture of ether and acetic ether (ether alone would not dissolve the morphine). On standing, the ethereal liquid rises to the surface: it is carefully removed, evaporated to dryness, and the residue tested or further purified in the manner described in the preceding paragraph.

The examination for morphine must be conducted with great care, and with as large a quantity of material as can be spared; for its isolation from other organic matter is an operation of difficulty, especially when only a minute proportion of alkaloid is present. Fortunately the detection of meconic acid does not involve similar difficulties; and as its reactions are quite characteristic, its presence is held to be strong evidence of the existence of opium in an organic mixture.

Examination for other Poisonous Alkaloids.

Stas's Process.—Minutely subdivide any solid matter; to this and the liquid portion of the vomit, etc., add about twice their weight of alcohol (90 or 95 per cent.) containing sufficient tartaric acid to fairly acidify the mixture. Digest the whole in a flask at a temperature of 150° to 160° F. (65·5° to 71° C.); set aside to cool; filter. The solution, which will contain the whole of the alkaloid, should then be evaporated nearly to dryness *in vacuo*, or at all events at a temperature not exceeding 100° F. (37·7° C.), lest volatile alkaloids should be dissipated. The residue is next exhausted with cold absolute alcohol; filtered; and the filtrate evaporated to dryness with the precautions already stated. The extract is dissolved in a very small quantity of water, treated with excess of powdered sodium or potassium bicarbonate, and well shaken with five or six times its volume of pure ether (with perhaps a little acetic ether). This ethereal liquid contains the alkaloid. Small portions should be evaporated in watch-glasses and tasted, or tested physically and chemically, according as the knowledge of collateral circumstances by the operator, or his experience, or such reactions as are recorded on pp. 613-632 may suggest.

If a volatile alkaloid (conine, nicotine, lobeline, sparteine) is indicated, the ethereal solution, which may contain animal matter, is removed, agitated with aqueous solution of caustic potash, decanted, and shaken with dilute sulphuric acid. On standing, the aqueous portion, containing the alkaloid as acid sulphate, subsides; the upper ethereal portion containing the animal matter is rejected; the acid aqueous liquid is made alkaline with caustic potash or soda; ether is added, and the whole well shaken; the ethereal liquid is decanted, evaporated to dryness *in vacuo*, or at a low temperature, and (to get rid of all traces of ammonia) again moistened with ether and dried. The residue is now tested for the suspected alkaloid by taste, smell, and the application of appropriate reagents (pp. 613-632).

If a non-volatile alkaloid (aconitine, atropine, brucine, colchicine, emetine, hyoscyamine, physostigmine, solanine, veratrine, as well as morphine, codeine, and strychnine, etc.) is indicated, further purify by decanting the ethereal liquid from the lower aqueous solution of sodium bicarbonate, removing the ether by evaporation, digesting the residue in alcohol, filtering, evaporating the alcohol, treating the residue with dilute sulphuric acid, setting aside for a few hours, filtering, concentrating, adding powdered potassium carbonate, and finally anhydrous alcohol. The alcoholic liquid, on evaporation, yields the alkaloid in a fit condition for testing in the manner already stated.

Sonnenschein's Process.—Digest with dilute hydrochloric acid, evaporate to the consistence of syrup, dilute, set aside for some hours, filter. Add solution of phosphomolybdic acid so long as any precipitate is produced, or cloudiness appears; collect the precipitate on a small filter; wash it with water containing phosphomolybdic and nitric acids, and, while still moist, place it in a flask. Decompose this compound of phosphomolybdic acid and alkaloid by adding caustic baryta until the stirred mixture is distinctly alkaline. Distil off volatile alkaloids, condensing and collecting these by help of a long tube so bent that the apparatus shall act as a retort, the end of the tube being attached to a bulb or a series of bulbs containing dilute hydrochloric acid. The acid liquid yields on evaporation a residue of hydrochlorides of alkaloids. The latter will afford characteristic reactions with the tests for the suspected alkaloid, and, on being moistened with baryta-water and warmed, will afford fumes of volatile alkaloids the odour of which is usually characteristic. The residue in the flask will contain non-volatile alkaloids. It is treated with carbonic anhydride to neutralize and precipitate the excess of baryta as insoluble barium carbonate; the mixture is evaporated to dryness over a water-bath; and the residue digested in alcohol. The alcoholic solution evaporated generally yields the alkaloids in a fit state for testing.

Reagents for Alkaloids.

Phosphomolybdic acid forms with ammonium salts, in nitric acid solution, a remarkably insoluble compound; and it behaves in a similar manner with salts of those compounds which are more or less analogous to ammonia—the nitrogenous organic bases—consequently forming an excellent reagent for their detection. It may be prepared in the following manner: A solution of ammonium molybdate is mixed with sodium phosphate, whereby a precipitate of ammonium phosphomolybdate is produced; the yellow precipitate, having been washed, is diffused through water, and heated with sufficient sodium carbonate to dissolve it. The solution is then evaporated to dryness, and calcined to drive off the ammonia. In case any of the molybdic compound be reduced by this operation, the residue must be moistened with nitric acid, and again calcined. The dry mass is then dissolved in cold water, the solution strongly acidulated with nitric acid, and water added until ten parts of the solution contain one of the dry salt. The liquid, which is of a golden-yellow colour, must be preserved from contact with ammoniacal fumes. It precipitates all the alkaloids (with the exception of urea) when a mere trace only is present. The precipitates are yellow, generally flocculent, insoluble in water, alcohol, ether, and dilute mineral acids, with the exception of phosphoric acid. Nitric, acetic, and oxalic acids, concentrated and boiling, dissolve them. These compounds are decomposed by the alkalies, certain metallic oxides, and the alkali-metal salts, which separate the alkaloid. To give an idea of the sensitiveness of this reagent, it may be stated that 0·000071 gramme of strychnine gives an appreciable precipitate with one cubic centimetre of the solution of phosphomolybdic acid.

Phosphoantimonic and phosphotungstic acids are also precipitants of alkaloids. Platinum, iridium, palladium, and gold chlorides are occasionally serviceable. Tannic and picric acids, too, may be used, and a solution of iodine and potassium iodide.

Other special reagents for alkaloids are "Mayer's"; "Nessler's" (*see* p. 718); the double potassium and cadmium iodide; and a solution of the double potassium and bismuth iodide. The latter is made (by Thresh) by mixing together one ounce of *Liquor Bismuthi*, B.P., 90 grains of potassium iodide, and 90 grains of concentrated hydrochloric acid. This orange-coloured solution gives a red precipitate with dilute cold solutions containing alkaloids.

Ptomaines (πτῶμα, a corpse) have already been alluded to as including poisonous alkaloids producible from putrefying animal matters, even the human body itself, during the ordinary processes of decay. They are distinguished, according to Brouardel and Boutmy, by a drop or two of a solution of their sulphate converting a drop of solution of potassium ferricyanide into ferrocyanide, the mixture then giving a dark-blue precipitate with a ferric salt. Some other substances also, as morphine, possess this converting power.

Tyrotoxicon.—This ptomaine (p. 594) may be isolated and tested as follows: Prepare an aqueous extract of the cheese, or filter the coagulated milk, etc. No heat should be applied, and undue exposure to air should be avoided by using stoppered bottles. Make the filtered fluid faintly alkaline with sodium carbonate, and well shake with half its bulk of ether. Allow the perfectly clear separated ethereal solution to evaporate spontaneously; and, if necessary, again extract the resulting aqueous residue with water, shaking with ether, evaporating as before, and testing the residue in two or three ways. A little placed on the tongue and swallowed will cause more or less of nausea, vomiting, purging, and headache. Again, the residue is either characteristically crystalline, or will become so after standing in a vacuum over sulphuric acid. Mix two or three drops of sulphuric acid and carbolic acid on a white plate, and add a few drops of the aqueous residue just mentioned; if an orange-red or purple colour results, the presence of tyrotoxicon may be suspected, but any nitrate or nitrite present may cause a similar colour. To some of the aqueous residue add an equal volume of a saturated solution of caustic potash; the double potassium and diazobenzene hydroxide is then formed and appears in six-sided plates, whereas any potassium nitrate appears in prisms. This residue may be treated with absolute alcohol, filtered, and the filtrate evaporated, when the plates may again be observed or the colour reaction again obtained with this purified product (Vaughan).

"Chloral Hydrate," p. 523, and "Chloroform," p. 459, are now included in "Part 2 of Schedule A" as "poisons within the meaning of the Pharmacy Act, 1868." "Cantharides" is in "Part 1." Its active principle is isolated as described on page 549, and is recognized by its blistering action on the less exposed portions of the skin.

ANTIDOTES.—*See* "Antidotes" in the Index.

QUESTIONS AND EXERCISES

In examining food and similar matter for poison, why must not the ordinary tests for the poison be at once applied?—What preliminary operations should be performed on a vomit in a case of suspected poisoning?—How would you search for corrosive sublimate in wine?—By what series of operations would you satisfy yourself of the presence or absence of arsenic in the contents of the stomach?—Describe the treatment to which decoction of coffee should be subjected in testing it for tartar-emetic.—State how the occurrence of lead in water is demonstrated.—Give a process for the detection of copper in jam.—How would you detect zinc in a vomit?—How may the presence of much sulphuric acid in gin be proved?—In testing ale for nitric acid what reactions would you select?—Show how you would conclude that a dangerous quantity of hydrochloric acid had been added to cider.—Describe the manipulations necessary in testing for hydrocyanic acid in the contents of a stomach.—By what method is oxalic acid discovered in infusion of coffee?—How is phosphorus detected in organic mixtures?—Give the process by which strychnine is isolated from a vomit.—Mention the experiments by which the presence of laudanum in porter is demonstrated.—Name the antidotes in cases of poisoning by:—*a*, alkaloids; *b*, antimonials; *c*, arsenic; *d*, barium salts; *e*, copper compounds; *f*, hydrochloric acid; *g*, hydrocyanic acid; *h*, lead salts; *i*, corrosive sublimate; *j*, nitric acid; *k*, oxalic acid; *l*, silver salts; *m*, oil of vitriol; *n*, tin liquors; *o*, zinc salts; *p*, carbolic acid.

EXAMINATION OF URINE AND CALCULI

The various products of the natural and continuous decay of animal tissue and the refuse matter of food are eliminated from the system chiefly as fæces, urine, and expired air. Air exhaled from the lungs carries off from the blood much carbon (about 8 ozs. in 24 hours) in the form of carbonic anhydride, and some aqueous vapour—the latter, together with a small amount of oily matter, also escaping by the skin. Directing the breath to a cold surface renders moisture evident; and breathing through a tube into lime-water demonstrates the presence of a considerable quantity of carbonic anhydride. The fæces consist mainly of insoluble *débris* of the food, mucus from the intestine, and residues from the biliary and other intestinal secretions, the soluble matters and water forming the urine. These excretions vary considerably, according to the food and general habits of the individual and the external temperature. But in disease the variations become excessive; hence their detection by the medical practitioner, or by the pharmacist for the medical man, is a matter of importance.

An analysis of fæces or air cannot be made with sufficient ease and rapidity to be practically available in medical diagnosis. But with regard to urine, certain abnormal substances and abnormal quantities of normal constituents may be chemically detected in the course of a few minutes by any one having already some knowledge of chemical and microscopical manipulation.

The total amount of urine voided daily under normal conditions varies considerably, the chief factors in causing variation being the amount of fluid taken into the body, and the temperature of the surroundings which causes inverse changes in the quantities of water removed by the skin, and in the expired air. The average daily output may be placed at two to three pints in the adult (1000 to 1500 c.c.).

The amount and character of the solid constituents of urine vary with the character and quantity of the diet, and the amount of muscular work and corresponding tissue changes. The average amount of total solids is usually given at 70 grammes per diem, of which 40 grammes consist of organic matter and 30 grammes of inorganic salts. The composition of the solids may be stated in round numbers, in grammes, as follows:—urea 33, creatinine 0·9, uric acid 0·5, hippuric acid 0·4, pigment and other organic substances 10, chlorine 7·5, sulphuric acid (SO_3) 2, phosphoric acid (P_2O_5) 3, sodium 11, potassium 2·5, calcium, magnesium, and ammonium 1·2.

The urea which is present to a considerable extent in urine, is the form in which the most of the waste nitrogen is eliminated from the system. Its empirical form is CON_2H_4. Its structural formula may be written, $CO\begin{cases}NH_2\\NH_2\end{cases}$; that is, it may be regarded as carbamide or as one of the organic bases already referred to, a primary diamine, in which the bivalent radical CO occupies the place of H_2. The other atoms of hydrogen may be displaced by various radicals, and many *compound ureas* thus be obtained.

Artificial Urea.—Urea may be prepared artificially by Williams's modification of Wöhler's method. Potassium cyanide, of the best commercial quality (containing about 90 per cent. of real cyanide), is fused at a very low red heat in a shallow iron vessel; red lead is added in small quantities at a time, the temperature being kept down by constant stirring. When the red lead ceases to cause further action, the mixture (potassium cyanate and lead) is allowed to cool, the product finely powdered, exhausted with cold water, barium nitrate added till no more precipitate (barium carbonate) falls, the mixture filtered, and the filtrate treated with lead nitrate so long as lead cyanate is thrown down. The latter is thoroughly washed, and dried at a low temperature. Equivalent quantities of lead cyanate and ammonium sulphate digested in a small quantity of water at a gentle heat (*see* p. 370) and filtered, yield a solution from which urea crystallizes on cooling.

Another process.—Basaroff has found that urea is produced when ordinary ammonium carbonate is heated in *strong* hermetically sealed tubes to about 275° F. (135° C.) for a few hours. The same chemist had previously obtained urea by similarly heating pure ammonium carbamate; so that the source of the urea in the former case is probably the ammonium carbamate believed to occur in the carbonate (*see* p. 98).

$$NH_4NH_2CO_2 - H_2O = CO(NH_2)_2$$

Tests for Urea.—1. Crystals of urea, cautiously heated in a test-tube, give an odour of ammonia, and a substance called *biuret* is formed, which, when dissolved in water, gives a rose red colour on adding a trace of cupric sulphate and excess of caustic potash.

2. Concentrated solutions of urea, such as are obtained by evaporating normal urine to one-fourth of its bulk, give with an equal volume of concentrated nitric acid an abundant crop of crystals of urea nitrate, in octahedra and hexagonal prisms. Oxalic acid under similar conditions yields flat-rhombohedral prisms.

3. Nitrous acid or hypobromites give a brisk effervescence of nitrogen.

4. Caustic alkalies cause an evolution of ammonia. A similar production of ammonia is caused by several micro-organisms, notably *micrococcus ureæ* which is the cause of the decomposition of urea, with evolution of ammonia, observed in stale urine. An enzyme has been isolated from this organism which also decomposes urea with evolution of ammonia.

Physical Examination of Urine

Normal urine varies in colour from a light straw yellow to dark brown, the average being a golden yellow. The pigment present in largest quantity and to which the normal colour of urine is almost wholly due is *urochrome*. The other pigments present are, *urobilin, uroerythrin,* and *hæmatoporphyrin.* The presence of blood causes a variation in colour from a slight smoky brown to a deep red according to the amount of blood. Bile gives the urine a greenish-brown colour. Both colour and odour are much influenced by certain kinds of food and by some drugs. Thus santonin and chrysophanic acid colour the urine orange. To distinguish these add caustic soda, which gives a red colour; shake with amyl alcohol, when the colour if due to santonin dissolves in the alcohol and then, in contact with air, changes to yellow; the colour due to chrysophanic acid does not dissolve in the amyl alcohol or only in traces (Hoppe-Seyler). The odour of diabetic urine not infrequently is that of acetone, from the presence of that substance. Many drugs, for example, cubebs, and some foods, as asparagus, give special odours to urine.

Fresh urine is clear. Any turbidity may be due to urates, phosphates, fat-globules, or pus. Urates redissolve when the urine is warmed; phosphates by the addition of acetic acid; pus and fat are detected by the microscope, *vide infra*. If the urine be turbid from the presence of phosphates when first voided, it may be due to conversion of urea into ammonium carbonate, which precipitates the phosphates within the bladder, in which case the fresh and warm urine will effervesce slightly on the addition of acetic acid. This condition is abnormal.

On standing, healthy urine commonly gives a slight cloud of mucus, and after severe exercise may give a sediment of urates.

The specific gravity of urine should be taken on a specimen removed from the whole bulk excreted in twenty or twenty-four hours; the normal specific gravity varies between 1·015 and 1·025. Many qualitative experiments and all quantitative operations should only be performed on the mixed urine of twenty-four hours.

Healthy urine when fresh is always slightly acid, the acidity being due to the presence of acid sodium phosphate. Alkalinity is probably due to that conversion of urea into ammonium carbonate within the bladder already described.

EXAMINATION OF MORBID URINE FOR ALBUMEN, SUGAR, BILE, BLOOD, EXCESS OF UREA, DEFICIENCY OF CHLORIDES, ETC.; AND URINARY SEDIMENT FOR URATES (OR LITHATES), PHOSPHATES, CALCIUM OXALATE, AND URIC ACID.

Albumen.—Faintly acidulate a portion of the clear urine in a test-tube with a few drops of dilute acetic acid (to keep phosphates in solution), and boil; flocks or coagula will separate if albumen be present. To detect small quantities, nearly fill a long test-tube with clear urine filtered if necessary, and faintly acidulated with acetic acid; then, holding the tube by its lower end, boil the upper portion of the urine.—A cloudiness in the boiled portion (as compared with the unboiled portion), which, on further addition of a few drops of acetic acid, does not disappear, indicates the presence of albumen.—Or, place a little nitric acid in a test-tube; then carefully pour down the side a little of the urine, so that it may lie above the acid. If albumen be present, an amorphous whitish ring or coagulum will, sooner or later, be formed at the junction of the fluids (Heller's test).

These experiments should first be made on normal urine containing a drop or two of solution of white of egg. The coagulum is white if it is only albumen, greenish if bile-pigment be present, and brownish-red if the urine contain blood. The influence of acids and alkalies on the precipitation of albumen is noticed on page 634.

A saturated solution of picric acid at once precipitates any albumen from urine. Should the urine be alkaline, it must be acidulated before applying this test. On warming the mixture, the precipitate will become more pronounced if due to the albumen or globulin of blood, or to any modifications of albumen caused by acidity or alkalinity of urine; but will disappear if due to peptone or propeptone. Potassium ferrocyanide, also, will precipitate the former varieties of albumen, but not the peptones.

Other forms of proteid.—Halliburton suggests the following sequence of operations for the detection of the various forms of proteid which may occasionally be present in abnormal urine. 1. If the urine gives no precipitate on boiling after acidulation, albumen and globulin are absent. If a precipitate occurs, albumen or globulin or both are present. 2. If the urine after neutralization gives no precipitate on saturation with magnesium sulphate, globulin and hetero-proteose are absent. If such a precipitate occurs, one or other is present. 3. If the urine be saturated with ammonium sulphate, filtered, and the filtrate gives no xanthoproteic or *biuret reaction*—a rose-red colour with cupric sulphate and a large excess of caustic potash—peptone is absent. 4. If the urine gives no precipitate on boiling after acidulation, no precipitate with nitric acid, and no precipitate on adding ammonium sulphate to saturation, peptone can be the only proteid present. Confirm this by the biuret reaction.

The occurrence of albumen in the urine may be temporary and of but little importance; or it may indicate the existence of a serious affection, known as Bright's disease. "Albumenuria is rarely a serious condition unless it is sufficiently pronounced to be made out by the cold nitric acid test" (Steward).

For quantitative purposes, Esbach employs the picric test, dissolving 10 parts of picric acid and 20 of citric acid in 900 of water, by aid of heat, and when the solution is cold, diluting with water to 1000 parts. This solution is added to a given volume of urine in a graduated Cetti's Esbach tube, and the height of the precipitate is noted after 24 hours. Johnson finds a simple solution of 5 grains of picric acid in 1 fluid ounce of water better than Esbach's solution, because the excess of acid in the latter tends to precipitate much uric acid which would be reckoned as albumen. If necessary, a standard value is given to the solution in the first instance by washing, drying and weighing the albumen.

A peculiar form of albuminuria called "Bence Jones Albumosuria" has now been described in a considerable number of cases. It is connected with a uniformly fatal multiple ulceration and softening of bone, and the proteid present is intermediate between albumen and the albumoses, being coagulable at a low temperature (60° C.) and redissolving to a great extent on boiling. It is also different from ordinary albumen in being readily soluble on boiling with hydrochloric acid.

Sugar.—To a portion of the clear urine in a test-tube add five to ten drops of solution of cupric sulphate; pour in solution of caustic potash or soda until the precipitate first formed is re-dissolved; slowly heat the solution to near the boiling-point; a yellow, yellowish-red, or red precipitate (cuprous oxide) is formed if sugar be present. (The production of a rose-red or pink tint with the cold alkaline cupric solution indicates the presence of albumoses or peptones.)

This experiment should first be made on urine containing a drop or two of solution of grape-sugar (p. 560). The cupric hydroxide precipitated by the alkali is insoluble in excess of pure caustic potash or soda, but readily dissolves if organic matter, especially sugar, be present. The cupric salt should not contain iron.

Other tests may be applied if necessary (*see* pp. 560 and 563). *See* also the Quantitative Determination of Sugar on p. 799. In any case in which, while the copper test points to sugar, medical diagnosis does not point to diabetes, the copper test should be checked by a fermentation test, for after the administration of chloral, camphor, morphine, phenol, and many other drugs, there may temporarily occur in the urine a compound termed *glycuronic acid,* which with the copper test affords a reaction identical with that of sugar.

Sugar is present in minute traces only in normal urine. In searching for small quantities, uric acid and creatinine, which also reduce the copper-solution, should first be removed by precipitation with solution of mercuric chloride (in the presence of sodium acetate, which promotes the precipitation), and removal of excess of mercury from the clear liquid by addition of ammonia. Normal urine rotates the plane of polarization of light slightly to the left, but if even a small amount of sugar be present, dextro-rotation results. In larger quantities (often 5 per cent.) sugar is a characteristic constituent of the urine of diabetic patients, greatly increasing the specific gravity of the secretion. Small hydrometers (termed *urinometers*) are commonly employed for ascertaining the specific gravity of urine.

Bile.—This is detected by the dark greenish-brown colour of the urine and by the general tests described on p. 643. In doubtful cases the urine should be thoroughly shaken up with a little chloroform, which dissolves the bile-pigments, and Gmelin's test applied to the separated chloroform. Oliver recommends that the urine be diluted to a sp. gr. of 1·008 and then one volume be added to three volumes of the following reagent, when more or less opalescence will be produced, according to the amount of bile acids present. For the reagent, dissolve 30 grains of flesh peptone, 4 grains of salicylic acid, and 33 minims of official acetic acid, in 8 ounces of water; filter.

Blood.—The presence of blood in the urine may be detected by the colour if the amount be not too small, by the spectroscope, or by the guaiacum test, which consists in the production of a blue colour when ozonic ether (made by adding hydrogen peroxide to ether) and tincture of guaiacum are added to the urine. This test is delicate, but is given by other substances, and ought to be confirmed by other tests.

Excess of Uric Acid.—A rough quantitative process consists in applying the qualitative method already described (p. 396) to a known volume of urine, and collecting on a filter, washing, and weighing the resulting uric acid. The result is always low. Hopkins *saturates* the urine with ammonium chloride, and, after a couple of hours, decomposes the separated ammonium urate by means of hydrochloric acid, and collects, washes, dries, and weighs the resulting uric acid. The normal yield should be roughly 0·3 to 0·5 per 1000. See *Proceedings of the Royal Society*, vol. lii., p. 93.

Excess of Urea.—About one-third of the solid matter in the urine is urea. Its proportion varies considerably; but 2 per cent. may be regarded as an average quantity. With regard to the amount of urea in urine, it is impossible to sharply define excess or deficiency. If nitric acid, added in equal volume, gives crystals without concentration, excess is certainly present in the sample examined: though, if the amount of urine passed in the twenty-four hours is much below the average, the total quantity of urea excreted may not be abnormal.

For quantitative determinations, the urine is treated in a suitable apparatus with an alkaline solution of recently prepared sodium hypobromite, and the nitrogen thus liberated is collected and measured. The reaction is of the following character:—

$$\underset{\text{Urea}}{CO(NH_2)_2} + \underset{\substack{\text{Sodium}\\\text{hypobromite}}}{3NaBrO} = \underset{\substack{\text{Sodium}\\\text{bromide}}}{3NaBr} + \underset{\substack{\text{Carbonic}\\\text{anhydride}}}{CO_2} + \underset{\text{Water}}{2H_2O} + \underset{\text{Nitrogen}}{N_2}$$

The carbonic anhydride represented in the equation is absorbed by the excess of alkali used in making up the hypobromite solution, so that only the nitrogen is evolved in gaseous form. Only about 94 per cent. of the nitrogen appears in gaseous form,* and allowance must be made for this deficiency if an instrument graduated in c.c.'s is employed for the determination. Usually, the instruments used clinically are, however, graduated in percentages, and in that case allowance is made in the initial graduation of the instrument.

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* In diabetic urine nearly the theoretical yield is obtained.

Many forms of instrument have been devised for determining the urea from the evolved nitrogen in this reaction, but they all fall into one of two classes, first that in which air is present over the hypobromite, with which the evolved nitrogen mixes and in which the amount of nitrogen is estimated from the increase in volume of the gas which is driven into a graduated cylinder; and, secondly, those in which the nitrogen is evolved alone in a graduated tube filled with the hypobromite solution. The principle of the first type of apparatus is shown in fig. 41 which has been constructed from ordinary laboratory apparatus. The burette fixed in the stand has air-tight connections above with the wide-mouthed bottle, and below with a funnel by means of rubber tubing. The burette is filled with water, which also fills the connecting tube and funnel to an equal level. The bottle contains 25 c.c. of the hypobromite solution, made by adding 2 c.c. of bromine to 23 c.c. of 40 per cent. solution of sodium hydroxide, and 5 c.c. of urine in a short wide test-tube are placed within the bottle, so that later, by tilting the bottle, the urine and hypobromite may be mixed. After placing the cork air-tight in the bottle, the level of the water in the burette is read, the water in the funnel being adjusted at an equal level, then the urine and hypobromite are mixed, and after an interval of ten minutes, the new level of the water is read. The difference in the readings gives the volume of nitrogen evolved; and 35·4 c.c. of nitrogen (measured at 18° C. and 760 mm. pressure) correspond to 0·1 gramme of urea, from which the percentage of urea can easily be calculated. Care must be taken to keep the temperature constant throughout the experiment by immersing the bottle in a bath of water, otherwise a large error will result from the change in volume of the contained air.

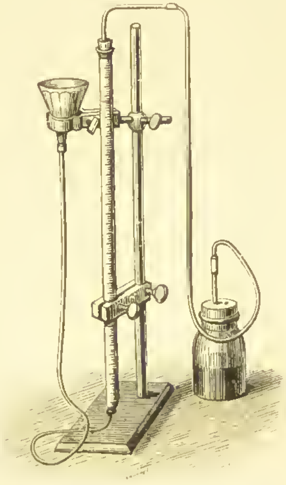


Fig. 41.

The other type of apparatus (Doremus Ureometer, fig. 42) is simpler and sufficiently accurate for all clinical purposes. The hypobromite solution is made to completely fill a graduated tube closed at the upper end and bent in "U" form at the bottom, beyond the bend a bulb is blown to contain the hypobromite displaced from the tube, and a short length of tubing reaches above the bulb. The tube is filled and also the bend and lower part of the bulb, by first filling the bulb with the solution and then slowly inverting so as to displace the air, on again turning up the tube the hypobromite completely fills the graduated tube, bend, and lower part of bulb. One c.c. of urine is now introduced by means of a bent pipette graduated to deliver 1 c.c. and filled and emptied by means of a rubber bulb at its end. Care must be taken to introduce all the urine and yet not to blow in bubbles of air. In a recent modification the urine is added from a small graduated tube attached to the side of the hypobromite tube and separated from it by a stopcock. These instruments are usually graduated in percentages of urea to obviate calculations.

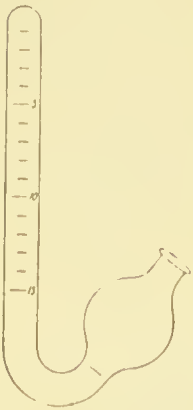


Fig. 42.
Doremus Ureometer.

In these instruments no error is introduced from changes in volume of admixed air, and although the quantity of urine used is small, they are fairly accurate.

A still more recent form of instrument for measuring small amounts of urea in blood or urine is that of Barcroft, in which the volume of gas and air is reduced to the same as that at the beginning, by applying pressure, and differences in pressure are measured instead of differences in volume.

It may be said of all these instruments that they do not measure the amount of urea with scientific accuracy, because, in the first place, all the urea-nitrogen is not given off; and, in the second, a small amount is set free from uric acid and other nitrogenous substances present in the urine, but for clinical purposes they give a very close approximation to the amount of urea present.

Chlorides.—Any ordinary sample of urine yields an abundant precipitate of silver chloride on the addition of nitric acid and silver nitrate. The amount of chlorides present may be determined by any of the usual methods for the determination of chlorides. The normal quantity of chlorine present as chlorides is 0·5 per cent.; but this may be reduced practically to *nil* in acute febrile conditions, such as pneumonia, partially from the stoppage of intake of chlorides in the food, and partially from increased metabolism of proteid binding the chlorides of the tissues, and blood, and lymph.

Chromogens.—Urine may contain chromogens. These are substances which do not at the time colour the urine, but which, on the addition of oxidizing reagents, or after standing some time, develop a colour. A blue colour may be seen in urine rich in indican on the addition of much nitric acid. This is due to the formation of indigo from its chromogen. The darkening often noticed on the addition of acid to urine is due to liberation of the urinary pigments from their chromogens.

Acetone in urine occurs usually in the later stages of *diabetes mellitus.* Halliburton thus describes a delicate test by Le Nobel. On adding an alkaline solution of sodium nitroprusside, so dilute as to have only a slight red tint, to a fluid containing acetone, a ruby-red colour is produced, which in a few moments changes to yellow, and on boiling, after adding acid, to greenish blue or violet.

The iodoform test for acetone consists in adding a small crystal of iodine, or a few drops of iodine dissolved in solution of potassium iodide, then a solution of a caustic alkali, and warming, when the odour of iodoform is obtained. Alcohol must not be present, so that the iodine must on no account be added as *Tinct. Iodi.*

The colour of urine. Caution.—Care must be taken not to confound the colour-changes in urine due to the action of drugs with the effects produced by the action of oxidizing agents on chromogens. Thus rhubarb, saffron, and santonin darken the natural yellow of urine, the addition of an alkali causing a red coloration. Carbolic acid taken internally, or absorbed from extensive wounds after surgical operations, makes the urine greenish black, resembling urine with much bile in it. If potassium iodide or bromide is being taken internally, the addition of a strong acid will often cause separation of iodine or bromine respectively in the urine. Medicinal astringents tend to reduce the normal colour of urine. Many soluble inorganic and organic medicinal substances pass out of the system with the urine, sometimes quite unchanged in character. *Pepsin* has been found in urine. "Small pieces of fibrin soaked in the urine absorb the pepsin therefrom; on removing them to 0·1 per cent. hydrochloric acid they are rapidly digested" (Leo).

Aceto-acetic acid is also found associated with acetone and β-oxy-butyric acid in diabetic urine. It may be detected by adding very dilute solution of ferric chloride cautiously drop by drop to the suspected urine. The first portion added precipitates the phosphates, which if present in excess may be filtered off. The first trace of ferric chloride after the phosphates have been precipitated gives a burgundy red colour, which disappears on heating the solution, and does not re-appear on cooling. This final stage of the test ought always to be performed, since it serves to distinguish the aceto-acetic acid from other substances which may be present, and give a similar result in the first part of the test, *i.e.* the colour reaction with ferric chloride in the cold.

URINARY SEDIMENTS

Warm the sediment with the supernatant urine, and filter.

<table>
<tr>
<td colspan="3"><i>Insoluble.</i>
Phosphates, calcium oxalate, and uric acid. Warm with acetic acid, and filter.</td>
<td rowspan="3"><i>Soluble.</i>
Ammonium, calcium, or sodium urates; chiefly the latter.
They are redeposited as the liquid cools, and if sufficient in quantity may be further examined for ammonium, calcium, sodium, and the uric acid radical by the appropriate tests.</td>
</tr>
<tr>
<td colspan="2"><i>Insoluble.</i>
Calcium oxalate and uric acid. Warm with hydrochloric acid, filter.</td>
<td rowspan="2"><i>Soluble.</i>
Phosphates.
Add ammonia; white ppt. = calcium phosphate or ammonium magnesium phosphate, or both.</td>
</tr>
<tr>
<td><i>Insoluble.</i>
Uric acid.
Apply the murexid test (p. 397).</td>
<td><i>Soluble.</i>
Calcium Oxalate.
May be reprecipitated by ammonia.</td>
</tr>
</table>

Notes.—Urinary deposits are seldom of a complex character: the action of heat and acetic and hydrochloric acids generally at once indicates the character of the deposit, rendering filtration and precipitation unnecessary.

The Urates are often of a pink or red colour, owing to the presence of a pigment termed *uroerythrin* or *purpurin;* hence the common name of *red gravel* for such deposits. *Purpurin* is soluble in alcohol, and may be removed by dissolving the deposit by heating, and extracting with amyl alcohol. It is seldom necessary to determine whether the urate be that of ammonium, calcium, or sodium (*see* also Uric acid, p. 396). The deposited urate is a very acid urate (quadriurate) which slowly (more rapidly in urine diluted with water) breaks up into a less acid urate (biurate) and uric acid (Bence Jones), the supernatant urine becoming at the same time less acid owing to the formation of mono- from di-hydrogen phosphates. The presence in the urine of mono-hydrogen phosphates, is apparently (Roberts) what prevents this decomposition before the urine is exposed to the air.

Calcium phosphate and *ammonium magnesium phosphate* (NH_4MgPO_4) are usually both present in a phosphatic deposit, the magnesium salt forming the larger proportion. They may, if necessary, and if sufficient in quantity, be separated by collecting on a filter, washing, and boiling with solution of sodium carbonate. The calcium and magnesium carbonates thus formed are collected on a filter, washed, and dissolved in a drop or two of hydrochloric acid; ammonium chloride, ammonia, and ammonium carbonate are added, and the mixture boiled and filtered; any calcium originally present will then remain insoluble, as calcium carbonate; while any magnesium will be precipitated from the filtrate as ammonium magnesium phosphate on the addition of sodium phosphate, the mixture being also well stirred.—— The chief portion of excreted earthy phosphates is carried off by the fæces, that remaining in the urine being kept in solution by the influence of acid sodium phosphate and, frequently, lactic acid.——Occasionally, an hour or two after a hearty meal, the urine becomes sufficiently alkaline for the phosphates to be deposited, and the urine when passed is turbid from their presence.——The ammoniacal constituent of the ammonium magnesium salt does not occur normally, but is produced from urea as soon as urine becomes alkaline.

Calcium oxalate is seldom met with in excessive amounts, but very often in small quantities mixed with phosphates.

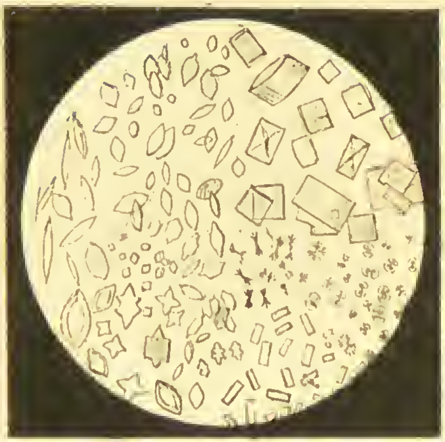
In the urine it is probably kept in solution by the influence of the acid sodium phosphate. In one case of oxaluria the whole urine excreted by a patient in twenty-four hours furnished to the author only two-thirds of a grain of calcium oxalate.

Free uric acid is in most cases distinctly crystalline, and nearly always of a yellow, red, or brown colour owing to the presence of impurities.

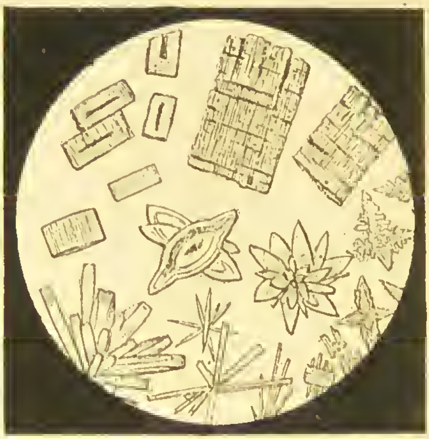
Artificial sediments.—For educational practice, these may be obtained as follows:—1. Triturate in a mortar a few grains of serpent's excrement (chiefly ammonium urate) with an ounce or two of urine; this represents a sediment of urates. 2. Add a few drops of solution of ammonia or solution of ammonium carbonate to urine; the deposit may be regarded as one of phosphates. 3. To an ounce or two of urine add very small quantities of calcium chloride and ammonium oxalate; the precipitate is calcium oxalate. 4. To urine acidulated with hydrochloric acid add a little serpent's excrement; the sediment is uric acid.

Other deposits than the foregoing are occasionally observed. Thus *hippuric acid,* $HC_9H_8NO_3$, a normal constituent of human urine and largely contained in the urine of herbivorous animals, is sometimes found associated with uric acid in urinary sediments, especially in those from patients whose medicine contains benzoic acid (p. 371). Its appearance, as observed by aid of the microscope, is characteristic—namely, slender, four-sided prisms, having pointed ends. *Cystin,* $C_3H_7NSO_2$ (from *κύστις, kustis,* a bladder, in allusion to its origin) rarely occurs as a deposit in urine. It is not soluble in warm urine or dilute acetic acid, and scarcely in dilute hydrochloric acid—hence would be met with in testing for free uric acid. It is very soluble in ammonia, recrystallizing from a drop of the solution placed on a piece of glass in characteristic microscopic six-sided plates. It communicates an odour, as of sweet briar, to fresh urine, soon changing to a most unpleasant smell. *Leucine* and *tyrosine* (*see* p. 593) are occasionally met with in cases of phosphorus poisoning and of acute yellow atrophy of the liver. As a rule they occur together in the form of small round yellowish masses of radiating crystals. *Organized sediments* may be due to the corpuscles of pus, mucus, or blood, fat-globules, spermatozoa, cylindrical casts of the tubes of the kidneys, epithelial cells

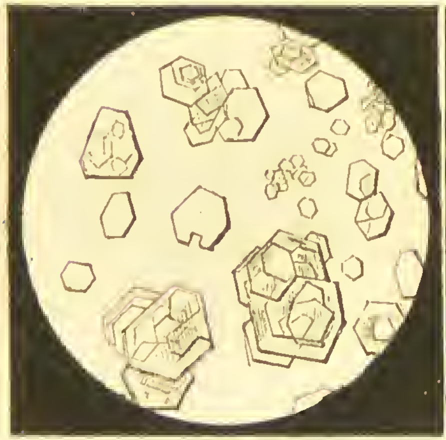
URINARY DEPOSITS (UNORGANIZED)



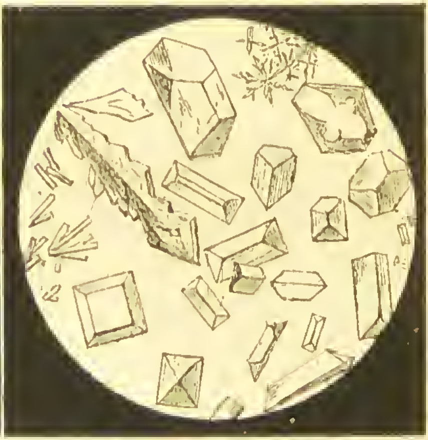
URIC ACID



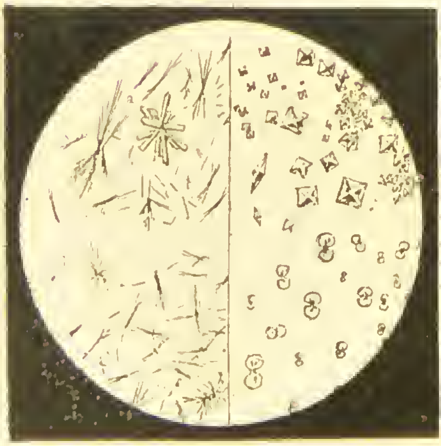
URIC ACID



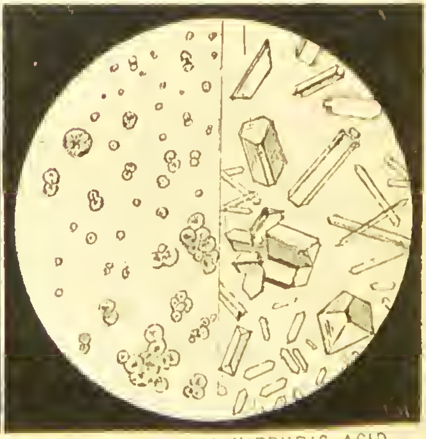
CYSTIN



TRIPLE PHOSPHATE



URATES, a. of Sodium, b, of Magnesium. OXALATE of CALCIUM.

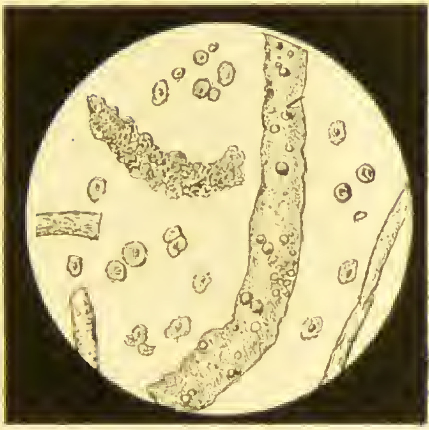


CARB OF CALCIUM HIPPURIC ACID

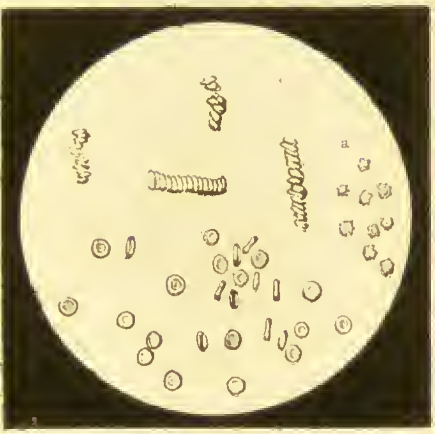
As seen with a ⅔ inch objective & N° 1 eye piece i e magnified 60 diam^{s}

Pl II

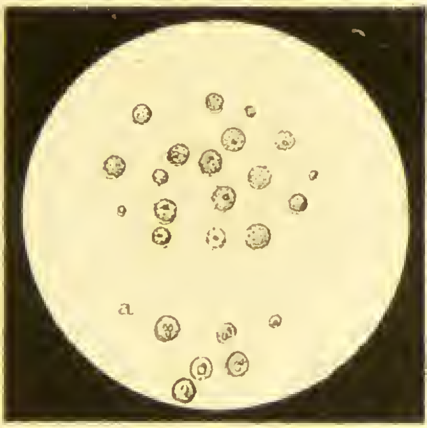
URINARY DEPOSITS (ORGANIZED)



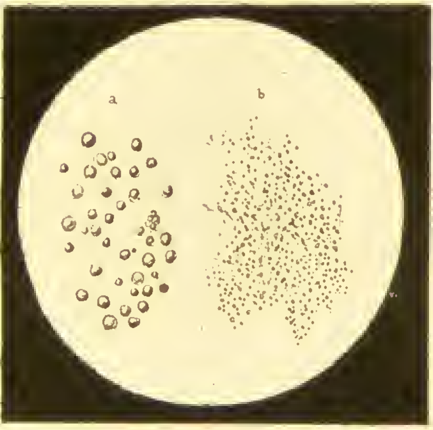
EPITHELIAL CELLS & TUBULI



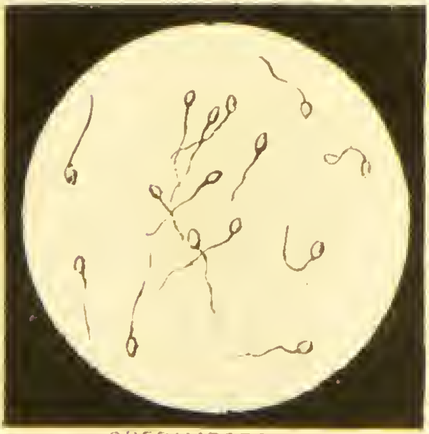
BLOOD. CORPUSCLES



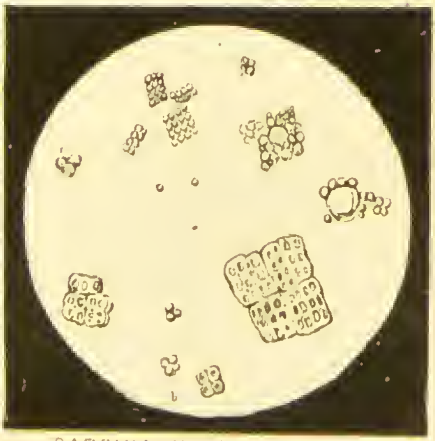
PUS. CORPUSCLES



FAT GLOBULES.



SPERMATOZOA



SARCINA VENTRICULI

As seen with a ¼ inch objective & N° 1 eye piece i.e. magnified 230 diam.

H B Brady del ad nat Tuffen West sc

from the walls of the bladder, or foreign matters, such as fibres of wool, or of cotton or wood, small feathers, dust, starch, etc.; these are best recognised by the microscope. (*See* the accompanying Plates, and the following paragraphs on the microscopic appearances of both crystalline and organized urinary sediments.)

Microscopic Examination of Urinary Sediments

Urine containing insoluble matter is usually more or less opaque. For microscopical examination a few ounces should be set aside in a conical test-glass for an hour or two, the clear supernatant urine poured off from the sediment as far as possible, a small drop of the residue placed on a slip of glass, covered with a cover-slip, and examined under the microscope with different magnifying powers.

> The respective appearances of the various crystalline and organized matters are given in the annexed lithograph Plates, the figures of which were kindly drawn by the late H. B. Brady, F.R.S., from natural specimens in the collections of St Bartholomew's Hospital, Dr Sedgwick, the late Mr W. W. Stoddart, Mr Waddington, and the Author.

Uric acid occurs in many forms, most of which are given in the first Plate. Flat more or less oval crystals, sometimes attached to each other, their outline then resembling an 8, a cross, or a star, are common. Single and grouped quadratic prisms, aigrettes, spicula, and crystals recalling dumb-bells are met with. From urine acidulated with hydrochloric acid, bundles or sheaves of square crystals, two opposite sides smooth and two jagged, are generally deposited: acidulated with acetic acid, more typical forms are obtained. A drop of solution of caustic potash or soda placed on the glass slip will dissolve a deposit of uric acid, a drop of any acid reprecipitating it in minute but characteristic crystals.

Cystin is very rarely met with as an urinary deposit; that from which the figure on Plate I. was taken was found in the urine of a patient in St Bartholomew's Hospital. Lamellæ of cystin always assume the hexagonal character; but the angles are sometimes ill defined and the plates superposed: in the latter case, a drop of solution of ammonia placed on the glass at once dissolves the deposit, well-marked six-sided crystals appearing as the drop dries up.

Triple phosphate (ammonium magnesium phosphate) is deposited as soon as urine becomes alkaline, the ammoniacal constituent being furnished by the decomposition of urea. It occurs in large prismatic crystals, forming a beautiful object when viewed by polarized light,—sometimes also in ragged stellate or arborescent crystals, resembling those of snow. Both forms may be artificially prepared by adding a small lump of ammonium carbonate to a few ounces of urine and setting aside in a test-glass.

Amorphous deposits are either *earthy phosphates* (a mixture of magnesium and calcium phosphates) or *urates* of calcium, magnesium, ammonium, potassium, or sodium—chiefly the latter. They may be distinguished by the action of a drop of acetic acid placed near the sediment on the glass slip, the effect on mixing being watched under the microscope; phosphates dissolve, while urates gradually give rise to characteristic forms of uric acid. Urates redissolve when warmed with the supernatant urine.

Sodium and magnesium urates, though generally amorphous, occasionally take a crystalline form—bundles or tufts of small needles—as shown in the Plate. When pink or brick-red, the colour is due to uroerythrin.

Calcium oxalate commonly occurs in octahedra requiring high magnifying-power for their detection. The crystals are easily overlooked if other matters are present, but are more distinctly seen after phosphates have been removed by acetic acid. In certain aspects the smaller crystals look like square plates traversed by a cross. A dumb-bell form of this deposit is also sometimes seen, resembling certain forms of uric acid and the coalescing spherules of a much rarer sediment—calcium carbonate. Calcium oxalate is insoluble in acetic but soluble in hydrochloric acid. The octahedra are frequently met with in the urine of persons who have partaken of garden rhubarb and certain other vegetables. The crystals may often be deposited artificially (according to Waddington) by dropping a fragment of oxalic acid into several ounces of urine and setting aside for a few hours.

Calcium carbonate is rarely found in the urine of man, but frequently in that of the horse and other herbivorous animals. Human urine containing calcium carbonate often reddens litmus-paper; and it is only after the removal, on standing, of the excess of carbonic acid, that the salt is deposited. It consists of minute spherules, varying in size, the smaller ones often in process of coalescence. The dumb-bell form thus produced is easily distinguished from similar groups of uric acid or calcium oxalate by showing a black cross in each spherule when viewed by polarized light. Acetic acid dissolves calcium carbonate, liberating carbonic anhydride with visible effervescence (under the microscope) if the slide has been previously warmed and a group of crystals be attacked.

Hippuric acid.—The pointed rhombic prisms and acicular crystals are characteristic and easily recognized. The broader crystals may possibly be mistaken for triple phosphate, and the narrower for certain forms of uric acid; but insolubility in acetic acid distinguishes them from the former, and solubility in alcohol from the latter. These tests may be applied while the deposit is under microscopic observation. An alcoholic solution of hippuric acid evaporated to dryness, and the residue treated with water, gives a solution from which characteristic crystalline forms of hippuric acid may be obtained on allowing a drop to dry on a slip of glass.

> Plate II. The organized deposits in urine entail greater care in their determination, and usually require a higher magnifying power for their proper examination than those of crystalline form. The figures on the second of the accompanying Plates are drawn to 230 diameters. The following notes will assist the observer.

Casts of uriniferous tubuli are of various forms, and often of considerable length—sometimes delicate and transparent, occasionally granular, and often beset with fat-globules. Epithelial *débris* are frequently present in urine in the form of nucleated cells, regular and oval when full, but angular and unsymmetrical when partially emptied of their contents—sometimes perfect, but more frequently broken up. Casts are very readily discovered by the use of the microscope, if, to a sample of the urine supposed to contain them, best in a conical glass, a few drops of an aniline dye be added. "Carbo-fuchsine" answers well. The casts rapidly stain, and are then quite easily seen in the field.

Blood corpuscles are readily identified under the microscope by their characteristic appearance; they are usually crenated when present; if the hæmoglobin has escaped, the stroma is often visible for some time, forming what is termed a shadow. The tests for blood, or rather hæmoglobin, in solution have already been described (*see* p. 675). It is noteworthy that when the blood is present in small quantities the spectrum obtained is that of methæmoglobin and not that of oxyhæmoglobin. When corpuscles are present, the condition is known as hæmaturia; when the blood colouring matter is in solution, as hæmoglobinuria.

It is not possible to state with certainty whether blood corpuscles found in urine are those of man, or of the domestic mammalia, for the slight differences in size are not sufficiently characteristic or fixed.

Pus and mucus.—Purulent urine deposits, on standing, a light-yellow layer, easily diffused through the liquid by shaking. Acetic acid does not dissolve the sediment; and *solution of caustic potash of official strength converts it into a gelatinous mass.* Under the microscope, pus-corpuscles appear rounded and colourless, rather larger than blood-discs, and somewhat granular on the surface. The corpuscles may be made more distinct by staining with a dilute solution of methylene blue. They generally show minute nuclei, which are more distinctly seen after treatment with acetic acid. (*See* the portion of the figure marked *a*.) Mucus possesses no definite microscopic characters, but commonly has imbedded in it pus, epithelium, and air-bubbles. Mucus is coagulated in a characteristic manner by acetic acid; and this reaction, together with the ropy appearance it imparts to urine, prevents it being confounded with pus.

Fatty matter (lipuria) occurs either as minute, highly refractile, glittering globules partially diffused through the urine (as shown at *a*) or in more intimate emulsion (as at *b* in the figure). When present in larger quantity, it collects as a sort of skim on the surface after standing.

Spermatozoa are liable to escape notice, on account of their small size and extreme transparency. Suspected urine should be allowed to settle some hours in a conical test-glass, and the drop at the bottom examined under a high power. The drawing shows their appearance. They become more apparent after staining by an anilin dye such as methylene blue.

Sarcinæ rarely occur in urine, but are not infrequent in vomited matters. The upper figures (*a*) are copied from Dr

Thudichum's drawing (from urine); the larger groupings (*b*) are from vomited matter.

Extraneous bodies, such as starch, hair, wool, fibres of cotton or of deal, or fragments of feathers, are often found in urinary deposits; and ludicrous mistakes have been made by observers not on their guard in respect to such casual admixtures.

EXAMINATION OF URINARY CALCULI

The term *calculus* is the diminutive of *calx,* a lime- or chalk-stone.

The following calculi have been met with:—(1) Uric acid, (2) Sodium urate, (3) Calcium oxalate (mulberry), (4) Fusible or mixed calcium and triple phosphates, (5) Calcium phosphate, (6) Calcium carbonate, (7) Xanthine, (8) Cystin, (9) Urostealith (fatty matter), (10) Indigo (one case).

Knowledge of the composition of a calculus or urinary deposit affords valuable diagnostic aid to the physician; hence the importance of a trustworthy analysis of these substances.

Nature of calculi.—Urinary calculi have the same composition as unorganized urinary sediments. They consist, in short, of sediments that have been deposited slowly within the bladder, particle on particle, layer on layer, the several substances becoming so compact as to be less easily acted on by reagents than when deposited after the urine has been passed—the urates less readily soluble in warm water, the calcium phosphate insoluble in acetic acid until it has been dissolved in hydrochloric acid and reprecipitated by an alkali.

Preliminary treatment.—If the calculus is whole, saw it in two through the centre, and notice whether it is built up of distinct layers or apparently consists of one substance. If the latter, use about a grain of the sawdust for analysis; if the former, carefully scrape off portions of each layer, and examine them separately. If the calculus is in fragments, select fair specimens of about half a grain or a grain each, and reduce to a fine powder by placing on a hard surface and crushing under the blade of a knife.

Analysis.—Commence the analysis by heating a portion, about the size of a pin's head, on platinum foil, in order to ascertain whether organic matter, inorganic matter, or both are present. If both, the ash is examined for inorganic substances, and a fresh portion of the calculus for uric acid by the murexid test. (In the absence of uric acid any slight charring may be considered to be due to indefinite organic matter.) If composed of organic matter only, the calculus will in nearly all cases be uric acid, the indication being confirmed by applying the murexid test in a watch-glass to another fragment, half the size of a small pin's head. If inorganic only, the ash on the platinum foil may be examined for phosphates, and a separate portion of the calculus for oxalates. Even a single drop of liquid obtained in any of these experiments may be filtered by placing it on a filter not larger than a sixpence and previously moistened with water, and adding three or four drops of water, one after the other as each passes through the paper; or a drop of the mixture may be placed on a fragment of damped filter-paper on a glass slide, the latter then tilted, and a clear drop be drained off from the paper on to the slide ready for the addition of a reagent. If the calculus is suspected to contain more than one substance, boil about a grain of the powder in half a test-tubeful of distilled water for a few minutes and pour it on a small filter; then proceed according to the following Table:—

<table>
<tr>
<td colspan="3"><i>Insoluble.</i>
Phosphates, calcium oxalate, and free uric acid. Boil with two or three drops of hydrochloric acid, and filter.</td>
<td rowspan="3"><i>Soluble.</i>
Urates.
These will probably be redeposited as the solution cools. Small quantities may be detected by evaporating the solution to dryness. They are tested for ammonium, sodium, calcium, and the uric acid radical by the appropriate reagents.</td>
</tr>
<tr>
<td rowspan="2"><i>Insoluble.</i>
Uric acid. Apply the murexid test (p. 397).</td>
<td colspan="2"><i>Soluble.</i>
Phosphates and calcium oxalate. Add excess of ammonia, and then excess of acetic acid; filter.</td>
</tr>
<tr>
<td><i>Insoluble.</i>
Calcium oxalate.</td>
<td><i>Soluble.</i>
Phosphates. They may be re-pptd. by ammonia.</td>
</tr>
</table>

Varieties of calculi.—Calculi composed entirely of *uric acid* are common; a minute portion heated on platinum foil chars, burns, and leaves scarcely a trace of ash. The phosphates frequently occur together, forming what is known as the *fusible calculus,* from the readiness with which a fragment aggregates, and even fuses to a bead, when heated on a loop of platinum wire in the blowpipe-flame. The phosphates may, if necessary, be examined further by the method described in connection with urinary deposits. Calcium oxalate often occurs alone, forming a dark-coloured calculus having a very rough surface, hence termed the *mulberry calculus.* Smaller calculi of the same substance are called, from their appearance, *hempseed calculi.* Calculi of *cystin* are rarely met with. *Xanthine* (from ξανθὸς, *xanthos,* yellow, in allusion to the colour it yields with nitric acid) still less often occurs as a calculus. The earthy concretions or "*chalk-stones,*" which frequently form in the joints of gouty persons are composed chiefly of biurates, the sodium salt being that most commonly met with. *Gall-stones,* or *biliary calculi,* occasionally form in the gall-bladder; they consist chiefly of *cholesterin* (from χολὴ, *cholē,* bile, and στερεὸς, *stereos,* solid), $C_{27}H_{45}OH$, which is chemically an alcohol, but in its solubilities resembles the fats; it is soluble in alcohol (90 per cent.) or ether, and crystallizes from such solutions in well-defined, square, scaly crystals which are characterized by possessing a notch at one corner. Phosphatic and other calculi of many pounds weight are occasionally found in the stomach and larger intestines of animals.

QUESTIONS AND EXERCISES

In breathing, how much carbon (in the form of carbonic anhydride) is exhaled from the lungs every twenty-four hours?—How may the presence of carbonic anhydride in expired air be demonstrated?—Mention an experiment showing the escape of moisture from the lungs during breathing.—State the method of testing for albumen in urine.—Give the tests for sugar in urine.—What is the average composition of healthy urine?—Give the tests for urea.—Write the rational formulæ of some compound ureas in which methyl or ethyl displaces hydrogen.—Describe an artificial process for the production of urea, giving equations.—Sketch out a plan for the chemical examination of urinary sediments.—A deposit is insoluble in the supernatant urine or in acetic acid; of what substances may it consist?—Which compounds are indicated when a deposit redissolves on warming it with the supernatant urine?—Name the salts insoluble in warmed urine, but dissolved on the addition of acetic acid.—Mention the chemical characters of cystin. At what stage of analysis would it be recognised?—Describe the microscopical appearances of the following urinary deposits:—uric acid, cystin, triple phosphate, earthy phosphates, urates, calcium oxalate, calcium carbonate, hippuric acid, tube-casts, epithelial *débris*, blood, pus, mucus, fat, spermatozoa, sarcinæ, extraneous bodies.—State the physical and chemical characters of urinary calculi.—How are urinary calculi prepared for chemical examination?—Construct a scheme for the chemical examination of urinary calculi.—What is the composition of "fusible calculus," and why is this calculus so-called?—State the characters of "mulberry" and "hempseed" calculi.—What are "chalk-stones" of gout, and "gall-stones" or "biliary calculi"?

THE GALENICAL PREPARATIONS OF THE BRITISH PHARMACOPŒIA

The preparation of Cerates, Confections, Decoctions, Enemas, Extracts, Glycerins, Infusions, Juices, Liniments, Lozenges, Mixtures, Ointments, Pills, Plasters, Poultices, Powders, Spirits, Suppositories, Syrups, Tinctures, and Wines, includes a number of mechanical rather than chemical operations, and belongs to the domain of pure Pharmacy. The medical or pharmaceutical student will probably have had some opportunity of practically studying these compounds before working at experimental chemistry, and may have prepared many of them according to the directions of the Pharmacopœia; if not, he is referred to the pages of the last edition of that work for details.

Among the Extracts, however, there are two (namely, those of Belladonna and Henbane) which are not simply evaporated infusions, decoctions, or tinctures, like most others, but are evaporated juices from which vegetable albumen, the supposed source of fermentation and decay, has been removed, and in which chlorophyll (the green colouring-matter of plant-juice) is retained practically unimpaired in tint. *See Extractum Belladonnæ Viride* and *Extractum Hyoscyami Viride* in B.P.

THE CHEMICAL PREPARATIONS OF THE BRITISH PHARMACOPŒIA

The process by which every official chemical substance is prepared has now been described, and the strictly chemical character of the processes has been illustrated by experiments and explained by aid of equations. Should the reader, in addition, desire an intimate acquaintance with those details of manipulation on which the successful and economic manufacture of chemical substances depends, he is advised to prepare, if he has not done so already, a few ounces of each of the salts mentioned in the British Pharmacopœia or commonly used in Pharmacy. A Dictionary or some of the larger text-books of Chemistry may also be consulted.

The production of many chemical and galenical substances on a commercial scale can only be successfully carried on in manufacturing laboratories, and with some knowledge of the circumstances of supply and demand, and of the value of raw material, by-products, etc.; for the technical preparation of such substances requires much knowledge beyond even a thorough acquaintance with chemistry. Still, in the present day, commercial Chemistry and Pharmacy can best hope for success when founded on the working out of abstract scientific principles. The problem of manufacturing success is now only solved with certainty by sound and wisely-applied science.

QUANTITATIVE MEASUREMENTS

Temperature

General Principles.—As a general rule, to which, however, there are some exceptions, substances expand when heated and contract when cooled, the alteration in volume being approximately constant and regular for equal increments or decrements of temperature. The extent of this alteration in a given substance, expressed in parts or degrees, constitutes the usual method of intelligibly stating with accuracy, precision, and minuteness a particular condition of warmth or temperature — that is, of sensible heat. The substance commonly employed for this purpose is mercury, the chief advantages of which are, that it will bear a moderately high temperature without boiling, a low temperature without freezing, does not adhere to glass to a sufficient extent to "wet" the sides of any tube in which it may be enclosed, and, from its good conducting-power for heat, responds rapidly to changes of temperature. Platinum, earthenware, alcohol, and air are also occasionally used for thermometric purposes.

The Thermometer.—The construction of an accurate thermometer is a matter of considerable difficulty; but the following are the leading steps in the operation. Select a piece of glass tubing having a fine capillary (*capillus*, a hair) bore, and about a foot long; heat one extremity in a blowpipe-flame until the orifice closes, and the glass is sufficiently soft to admit of a bulb being blown; heat the bulb to expel air, immediately plunging the open extremity of the tube into mercury; the bulb having cooled, and some mercury having entered and taken the place of expelled air, again heat the bulb and tube until the mercury boils and its vapour escapes through the bore of the tube; again plunge the extremity under mercury, which will probably now completely fill the bulb and tube. When cold, the bulb is placed in melting ice. The top of the column of mercury in the capillary tube should then be within an inch or two of the bulb; if higher, some of the mercury must be expelled by heat; if lower, more metal must be introduced as before. The tube is now heated near the open end and a portion drawn out, until the diameter is reduced to about one-tenth. The bulb is next warmed until the mercurial column rises above the constricted part of the tube, which is then rapidly fused in the blowpipe-flame, and the extremity of the tube removed.

The instrument is now ready for *graduation*. The bulb is placed in the steam just above some rapidly boiling water (a medium having, *cæteris paribus*, an invariable temperature), and when the position of the top of the mercurial column is constant (the flask containing the water and steam being jacketed to prevent loss of heat by radiation), a temporary mark is made on the stem to indicate this position. This operation is repeated with melting ice (also a medium having an invariable temperature). The space between these two marks is divided into a certain number of intervals termed *degrees.* Unfortunately, this number is not uniform in all countries: in Britain it is 180, as proposed by Fahrenheit; in France 100 (the Centigrade scale) as proposed by Celsius, a number generally adopted by scientific men : in some parts of the Continent the divisions are 80 for the same interval, as suggested by Réaumur. Whichever be the number selected, similar markings should be continued beyond the boiling and freezing points as far as the length of the stem admits. They may be etched permanently on the stem itself, or on any wood, metal, or earthenware frame on which the stem is mounted.

"Thermometers employed in taking Specific Gravities, Melting-Points, or Boiling-Points, should have been compared with a standard thermometer, and their errors recorded in a table, by means of which the readings of the instruments used are to be corrected. The zero-point of the instruments should be verified from time to time."—B.P., 1898.

In ascertaining the temperature of a liquid, the bulb of a thermometer is simply inserted and the degree noted. In determining the boiling-point, also, the bulb may be inserted in the liquid, if a pure substance. (*See* the official directions on the following page.) In taking the boiling-point of a substance which is being distilled from a mixture, the bulb of the thermometer should be in the vapour but not beneath nor very near to the surface of the boiling liquid.

The "boiling-point" of a liquid is the temperature at which the pressure of the vapour of the substance overcomes the atmospheric or other pressure to which the liquid is exposed. When the pressure is equal to 760 mm. (29·92 inches) of mercury, water boils at 100° C. (212° F.). The boiling-point of a drop of a fluid is taken by introducing it into the closed extremity of a small U tube, the remaining portion of the closed limb being filled with mercury. The tube is lowered into a bath, the open limb being above the surface of the fluid of the bath. The bath is slowly and equally heated, and the boiling-point of the liquid, indicated by the mercury falling until it is level in the two limbs, taken by a thermometer whose bulb is close to the U tube.

Determination of Boiling-Point.—"To determine the boiling-point of a substance, the liquid under examination should be placed in a distilling flask having a side tube for conveying the vapour to a condenser, while the thermometer passes through a cork inserted in the neck. The bulb of the thermometer should be near to, but not immersed in, the liquid, and the whole of the thread of mercury should, if possible, be surrounded by the vapour; the temperature is read off as soon as the liquid is distilling freely. If any considerable length of the mercurial column be not surrounded by the vapour, the temperature of the emergent column should be ascertained as directed under melting-points [*see* next page], and the necessary correction applied."—B.P., 1898.

The following are the boiling-points of a few substances met with in pharmacy:—

	Centigrade.	Fahrenheit.
Alcohol, absolute	78·3	173
,, amyl	132·2	270
Benzol	80·6	177
Bromine (below)	63	145·4
Benzoic acid (pure, 249° C.; 480·2° F.)	239·0	462
Carbolic acid (not higher than)	182	359·6
Chloroform	60 to 62	140 to 143·6
Ether (B.P.) (below)	40·5	105
,, purified (not below)	34·5	94·1
Mercury *in vacuo* (as in a thermometer)	304	580
,, in air (barom. at 30 inches)	350	662
Water (barom. at 29·92 inches)	100	212
,, (,, 29·33 ,,)	99·5	211
,, (,, 28·74 ,,)	99	210
Saturated solutions of:—		
Cream of tartar	101	214
Common salt	106·6	224
Sal-ammoniac	113·3	236
Sodium nitrate	119	246
,, acetate	124·4	256
Calcium chloride	179·4	355

Determination of Melting-Point.—To melt at a given temperature is a *constant* property of a substance; therefore a melting-point, once it is accurately determined, becomes a valuable indicator of purity in a substance. The official (B.P., 1898) description of the mode of making a melting-point determination is as follows:—"To determine the melting-point of a substance a minute fragment of it should be placed in a thin-walled glass tube having an internal diameter of about 1 millimetre ($\frac{1}{25}$ inch), and sealed at the lower end. This tube should be attached to the thermometer so that the substance is near the middle of the bulb, and the thermometer with the attached tube should be immersed in a suitable liquid, contained in a beaker placed over a small lamp flame. Water is suitable for substances melting below 212° F. (100° C.), sulphuric acid, hard paraffin, or glycerin for substances melting at higher temperatures. The liquid should be continually stirred by means of a glass ring moved up and down till the substance is seen to melt. The temperature is noted, the tube cooled till the substance solidifies, and the operation then repeated. The latter reading of the thermometer should be taken as the melting-point. To obtain accurate results, the whole of the mercury column of the thermometer should be immersed in the heated liquid, but as this is seldom practicable, the mean temperature of the emergent column—that is, of that portion above the surface of the heated liquid—should be ascertained and the necessary correction applied. To obtain the mean temperature of the emergent column, a small thermometer is fixed by india-rubber bands in such a position that its bulb is about the middle of the emergent column. The corrected temperature may be calculated with approximate accuracy from the formula:—

$$\text{Corrected Temperature} = T + \cdot 000143\,(T - t)\,N,$$

in which

T = observed, *i.e.* uncorrected, temperature;

t = mean temperature of the emergent column;
N = the length of the emergent column in scale degrees."

The following are melting-points of substances official in the British Pharmacopœia:—

	In degrees Centigrade.	In degrees Fahrenheit.
Acetic acid, glacial	15·5	60
,, ,, congeals at . .	1·1	34
Benzoic acid	121·4	250·5
Carbolic acid	38·8	102
Oil of theobroma . . (about)	32	90
Phosphorus	43·3	110
Prepared lard . . . (about)	38	100
,, suet	44·4 to 48·9	112 to 120
Spermaceti.	46 ,, 50	114·8 to 122
White wax	62·5 ,, 63·9	144·5 ,, 147
Yellow wax	62·5 ,, 63·9	144·5 ,, 147

Pyrometers.—Temperatures above the boiling-point of mercury are determined by ascertaining to what extent a bar of platinum or porcelain has elongated. The bar is enclosed in a cavity of a suitable case, a plug of platinum or porcelain placed at one end of the bar, and the whole exposed in the region the temperature of which is to be found. After cooling, the distance to which the bar has forced the plug along the cavity is accurately measured and the corresponding degree of temperature noted. The value of the distance is fixed for low temperatures by comparison with a mercurial thermometer, and the scale carried upwards through intervals of equivalent length. Such thermometers are conventionally distinguished from ordinary instruments by the name *pyrometer* (from πῦρ, *pur*, fire, and μέτρον, *metron*, measure).

The order of fusibility of a few of the metals is as follows:—

	In degrees Centigrade.	In degrees Fahrenheit.
Mercury	– 39·4	– 39
Potassium	+ 62·5	+ 144·5
Sodium	97·6	207·7
Tin	227·8	442
Bismuth	264	507
Lead	325	617
Zinc	411·6	773
Antimony	621	1150
Silver	1023	1873
Copper	1091	1996
Gold	1102	2016
Cast iron	1530	2786

QUESTIONS AND EXERCISES

On what general principles are thermometers constructed?—What material is employed in making thermometers?—Why is mercury selected as a thermometric indicator?—Describe the manufacture of a mercurial thermometer.—How are thermometers graduated?—State the boiling-points of alcohol, chloroform, ether, mercury, and water on either thermometric scale.—Describe the details of manipulation in determining the melting-points of solids.—In what respect do pyrometers differ from thermometers?—Mention the melting-points of glacial acetic acid, oil of theobroma, lard, suet, and wax.—Give the fusing-points of tin, lead, zinc, copper, and cast iron.

Weight

The Balance.—The balance used in the quantitative operations of chemistry must be accurate and sensitive. The points of suspension of the beam and pan should be polished steel or agate knife-edges, working on agate planes. It should turn easily and quickly, without too much oscillation, to $\frac{1}{500}$ or $\frac{1}{600}$ of a grain, or $\frac{1}{10}$ of a milligramme, when 1000 grains, or 50 or 60 grammes, are placed in each pan. (Grammes are weights of the metric system, a description of which is given on pages 29-32.) The beam should be light but strong, capable of supporting a load of 1500 grains or 100 grammes: its oscillations are observed by help of a long index attached to its centre, and continued downwards for some distance in front of the supporting pillar of the balance. The instrument should be provided with screws for purposes of adjustment, a mechanical contrivance for supporting the beam above its bearings when not in use or during the removal or addition of weights, spirit-levels to enable the operator to place the balance in a horizontal position, and the whole should be enclosed in a glass case to protect it from dust. It should be placed in a room the atmosphere of which is not liable to be contaminated by acid fumes, and in a situation as free as possible from vibration. During weighing, the doors of the balance-case should be shut, in order that currents of air may not unequally influence the pans.

The Weights.—These should be preserved in a box having a separate compartment for each weight. A weight should not be lifted directly with the fingers, but by the aid of a small pair of forceps. If grain-weights, they should range from 1000 grains to $\frac{1}{10}$ grain, with a $\frac{1}{10}$ made of gold wire to act as a "rider" on the divided beam, and thus indicate by its position 100ths and 1000ths of a grain. From $\frac{1}{10}$ to 10 grains the weights may be of platinum or aluminium; thence upwards to 1000 grains of gilt or platinized brass. The relation of the weights to each other should be decimal. Metric decimal weights may range from 100 grammes to 1 gramme of gilt or platinized brass, and thence downwards to 1 centigramme, of platinum or aluminium, a gold centigramme rider being employed to indicate milligrammes and tenths of a milligramme.

Specific Gravity or Relative Density

The *specific gravity*, or *relative density*, of a substance is the ratio of its weight to that of an equal volume of a standard substance. This comparative heaviness in the case of *solids and liquids* is conventionally expressed in relation to water: they are considered as being lighter or heavier than water. Thus, water being regarded as unity = 1, the relative density, or specific gravity, of ether is represented by the figures 0·720 (it is less than three-fourths, 0·750, the weight of water), oil of vitriol by 1·843 (it is nearly twice, 2·000, as heavy as water). The specific gravities of substances are, moreover, the weights of similar volumes *at sixty degrees* (60° F.; 15·5° C.); for the weight of a definite volume of any substance varies according to temperature, becoming, as a rule, heavier when cooled and lighter when heated, different substances (gases excepted) differing in the extent to which they contract and expand. While, then, *specific gravity* is, truly, the comparative weight of equal bulks, the numbers which, in Great Britain, commonly represent specific gravities are the comparative weights of equal bulks at 60° F. (15·5° C.), water being taken as unity.* The standard of comparison for gases was formerly air, but is now usually hydrogen.

Specific Gravity of Liquids

Procure any small bottle holding from 100 to 1000 grains, and having a narrow neck; counterpoise it in a delicate balance; fill it to about half-way up the neck with pure distilled water having a temperature of 60° F. (15·5° C.); ascertain the weight of the water, and, for convenience, add or subtract a drop or two, so that the weight shall be a round number of grains; mark the neck by the aid of a diamond or file-point at the level of the lower edge of the curved surface of the water. Consecutively fill up the bottle to this neck-mark with several other liquids, cooled or warmed to 60° F. (15·5° C.), first rinsing out the bottle once or twice with a small quantity of each liquid, and note the weights; the respective figures represent the relative weights of equal volumes of the liquids. If the capacity of the bottle is 100, or 1000 grains, the resulting weights will, without calculation, show the specific gravities of the liquids; if any other number, a simple calculation must be worked out to ascertain the weight of the liquids as compared with 1 (or 1·000) of

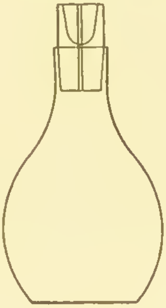


Fig. 43.

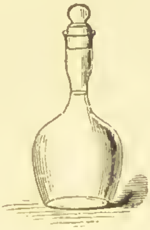


Fig. 44.

Specific Gravity Bottles.

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* The true weight of a substance is its weight in air plus the weight of an equal volume of air and minus the weight of a volume of air equal to the volume of the brass or other weights employed; or, in other words, its weight *in vacuo*, uninfluenced by the buoyancy of the air; but such a correction of the weight of a substance is seldom necessary, or, indeed, desirable.

water. Bottles conveniently adjusted to contain 250, 500, or 1000 grains, or 50 or 100 grammes of water, when filled to the top of their perforated stopper (fig. 43), and other forms of the instrument, are sold by all chemical-apparatus makers. Figure 44 is that of a bottle extremely useful in ascertaining the specific gravities of very volatile liquids.

Verify some of the following stated specific gravities of official liquids:—

Acid, acetic	1·044
,, ,, diluted	1·006
,, ,, glacial	1·058
,, carbolic	1·060 to 1·066
,, hydrochloric	1·160
,, ,, diluted	1·052
,, hydrocyanic	0·997
,, nitric	1·420
,, ,, diluted	1·101
,, nitro-hydrochloric	1·070
,, phosphoric, diluted	1·080
,, sulphuric	1·843
,, ,, aromatic	0·922 to 0·926
,, ,, diluted	1·094
,, sulphurous, solution of	1·025
Alcohol, absolute (real)	0·7935
,, ,, (official)	0·794 to 0·7969
,, (90 per cent.)	0·834
,, (45 ,,)	0·9436
Ammonia, aromatic spirit of	0·888 to 0·893
,, solution of	0·959
,, strong solution of	0·891
Benzol	0·880 to 0·888
Bismuth and ammonium citrate, solution of	1·070
Chloroform	1·490 to 1·495
Creosote	not below 1·079
Ether	0·735
,, purified	0·720 to 0·722
,, spirit of nitrous	0·838 to 0·842
Glycerin	1·260
Ferric acetate, solution of	1·031
,, chloride ,,	1·110
,, nitrate ,,	1·107
,, sulphate ,,	1·441
,, chloride, strong solution of	1·420
Lead subacetate, strong solution of	1·275
Lime, saccharated solution of	1·055
,, solution of chlorinated	1·055
Mercury (at 0° C. = 32° F.)	13·596
,, (at 15·5° C. = 60° F.)	13·560
,, nitrate, acid solution of	(about) 2·000

Oil of eucalyptus	0·910 to 0·930
,, mustard	1·018 to 1·030
,, sandal wood	0·975 to 0·980
Potash, solution of	1·058
Soda, ,, chlorinated	1·054
Squill, oxymel of	1·320
Syrup	1·330
,, of ferrous iodide	1·380 to 1·387

Hydrometers, formerly termed *areometers*.—The specific gravity of liquids may be ascertained, without balance and weights, by means of the *hydrometer*—an instrument usually of glass, having a graduated stem and a bulb or bulbs at the lower part. The specific gravity of a liquid is indicated by the depth to which the hydrometer sinks in the liquid, the point marked 1·0 or 1000 upon the scale indicating the depth to which it sinks in pure water. Hydrometers constructed for special purposes are known under the names of saccharometer, lactometer, elæometer, urinometer, alcoholometer. Hydrometers require a considerable quantity of liquid fairly to float them; and specific gravities observed with them are usually less delicate and trustworthy than those obtained by the balance, nevertheless they are exceedingly useful for many practical purposes where the employment of a delicate balance would be inadmissible.

SPECIFIC GRAVITY OF SOLIDS IN MASS

Weigh in the usual manner a piece (50 to 250 grains) of any solid substance heavier than water. Then weigh it in water, by suspending it from a shortened balance-pan by a fine hair or filament of silk and immersing in a vessel of water (fig. 45). The buoyant properties of the water will cause the solid apparently to lose weight; *this loss in weight is the exact weight of a volume of water equal to the volume of the immersed object.* The weight of the substance and the weight of an equal volume of water being thus ascertained, a simple calculation gives the relative weight of the sub-

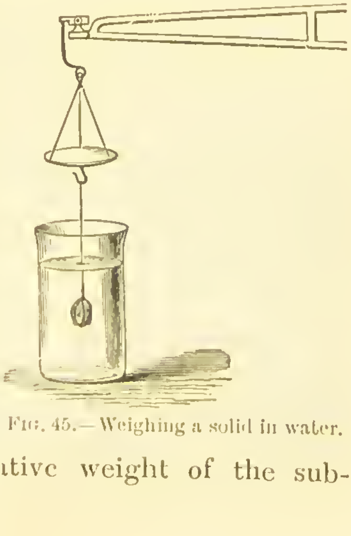

Fig. 45.—Weighing a solid in water.

stance, as compared with water = 1·000. Divide the weight in air by the loss of weight in water, the resulting number is the specific gravity in relation to 1 part of water, the conventional standard of comparison.

Verify some of the following specific gravities:—

Aluminium	2·56
Antimony	6·71
Bismuth	9·83
Coins, English, gold	17·69
,, ,, silver	10·30
,, ,, bronze	8·70
Copper	8·95
Gold	19·34
Iron	7·84
Lead	11·36
Magnesium	1·74
Marble	2·70
Phosphorus	1·77
Platinum	21·53
Silver	10·53
Sulphur	2·05
Tin	7·29
Zinc	7·14

Specific gravities of solid substances should be taken in water having a temperature of about 60° F. (15·5° C.). The substance should be immersed about half an inch below the surface of the water; adhering air-bubbles must be carefully removed; the substance must be quite insoluble in water.

Specific Gravity of Solids in Powder or Small Fragments

Weigh the particles; place them in a counterpoised specific-gravity bottle of known capacity, and filled up with water, taking care that the substance is thoroughly wetted; again weigh. From the combined weights of water and substance subtract the amount due to the substance: the residue is the weight of the water. Subtract this weight of water from the quantity which the bottle normally contains: the residue is the amount of water displaced by the substance. Having thus obtained the weights of equal volumes of water and substance, the specific gravity of the latter, as compared with water = 1·000, is obtained by dividing the weight of the substance by the weight of the water.

Or, suspend a cup, short glass tube, or bucket from a shortened balance-pan; immerse in water; counterpoise; place the weighed powder in the cup, and proceed as directed for taking the specific gravity of a solid in mass.

This operation may be conducted on fragments of any of the substances the specific gravities of which are given in the foregoing Table, or on the powdered piece of marble the specific gravity of which has been taken in mass. The specific gravity of one piece of glass, first in mass, then in powder, may be ascertained; the results should be identical. The specific gravity of shot is about 11·350; sand, 2·600; mercury, 13·56.

Specific Gravity of Solids Soluble in Water

Weigh a piece of sugar or other substance soluble in water; then suspend it from a balance in the usual manner, and weigh it in turpentine, benzol, or petroleum, the specific gravity of which is known or has been previously determined; the loss in weight is the weight of an equal volume of the turpentine, *i.e.*, it is the weight of the turpentine displaced by the substance. Ascertain the weight of an equal volume of water by calculation:—

$$\text{Sp. gr. of turpentine} : \text{sp. gr. of water} :: \text{weight of turpentine displaced} : \text{weight of an equal volume of water.}$$

The exact weights of equal volumes of sugar and water having been obtained, the specific gravity of sugar, as compared with water = 1·000 is obtained by calculation. Divide the weight of the sugar by that of the equal volume of water, the quotient is the specific gravity of sugar. The stated specific gravity of sugar ranges from 1·590 to 1·607.

Specific Gravity of Solids Lighter than Water

This is obtained in a manner similar to that for solids heavier than water; but the light substance is sunk by attaching it to a piece of heavy metal, the weight of water which the latter displaces being deducted from the weight displaced by both; the remainder is the weight of a quantity of water equal in volume to the light substance. For instance, a piece of wood weighing 12 grammes (or grains—for it is assumed that the student works equally well with metric as with imperial weights) is tied to a piece of metal weighing 22 grammes, the loss of weight of the metal in water previously having been found to be 3 grammes. The two, weighing 34 grammes, are now immersed, and the loss in weight is found to be 26 grammes. But of this loss 3 grammes have been proved to be due to the buoyant action of the water on the metal; the remaining 23, therefore, represent the same effect on the wood; 23 and 12, therefore, represent the weights of equal volumes of water and of the wood, and 23 : 12 : : 1 : 0·5217. Or, shortly, as before, divide the weight of the wood in air by the weight of an equal volume of water; 0·5217 is the specific gravity of the wood. Another specimen of wood may be found to be three-fourths (0·750) the weight of water, and others heavier. Cork varies from 0·100 to 0·300.

The specific gravity of a very minute quantity of a heavy or light substance may be ascertained by noting the specific gravity of a fluid in which it, being insoluble, neither sinks nor swims; or by immersing it in a weighed piece of paraffin whose specific gravity is known, noting the specific gravity of the whole, and correcting for the influence of the paraffin.

Specific Gravity of Gases

The determination is analogous to that in the case of liquids. A globe exhausted of air and holding from 1 to 4 litres (or quarts) is suspended from the arm of a balance, and counterpoised by a similar flask. Gases are introduced in succession and their weights noted. By calculation their specific gravities are obtained in relation to air or hydrogen, whichever is taken as a standard.

Correction of the Volume of Gases for Pressure.—The height of the barometer at the time of manipulation is noted.

Remembering that the volume which a gas occupies varies inversely as the pressure to which it is subjected (Boyle's Law, p. 36), a simple calculation shows the volume which the gas would occupy at 760 millimetres (or 29·92 inches), the standard pressure (30 inches is sometimes adopted as the standard in Britain).* Thus 40 volumes of a gas at 740 millimetres pressure are reduced to 39 when the pressure becomes 760 millimetres (or 90 vols. at 29 inches pressure become 87 vols. at 30 inches).

Correction of the Volume of Gases for Temperature.—This is done in order to ascertain what volume the gas would occupy at 0° C. (32° F.) or 15·5° C. (60° F.), according to the standard taken. Gases are equally affected by equal variations in temperature (Charles). They expand about 0·3665 † per cent. ($\frac{1}{273}$) of their volume *at the freezing-point of water* for every C. degree (0·2036 per cent., or $\frac{1}{491}$ for every F. degree) that their temperature is raised above that point (see Charles's Law, p. 37). Thus 8 volumes of gas at 0° C. will become 8·293 at 10° C.; for if 100 become 103·665 on being increased in temperature 10° C., 8 will become 8·293 (or if 100 become 102·036 on being increased 10° F., 8 will become 8·163).

Vapour-density.—Vapours are those gases which condense to liquids at ordinary temperatures. What is commonly called the vapour-density of a substance is really the specific gravity or *relative* density of its vapour, and is simply the ratio of the weight of any given volume to that of a similar volume of air or hydrogen at the same temperature and pressure. But, for convenience of comparison, this experimental specific gravity is referred, by calculation as just described for permanent gases, to a temperature of 0° C., and 760 millimetres pressure. A teaspoonful or so of liquid is placed in a weighed flask of about the capacity of a common tumbler and having a capillary neck: the flask is immersed in an oil-bath and heated to a temperature considerably above the boiling-point of the liquid; at the moment vapour ceases to escape, the neck is sealed by a blowpipe-flame, and the temperature of the bath noted; the flask is then removed, cooled, cleaned, and weighed; the height of the barometer is also taken. The neck of the flask is next broken off beneath the surface of water (or of mercury), which rushes in and fills it, and the flask is again weighed with its contents, by which its capacity in cubic centimetres is found. From these data the volume of vapour yielded by a given weight of liquid is ascertained by a few obvious calculations. The capacity of the globe having been ascertained, the weight of an equal volume of air[*] is calculated. This weight of air is deducted from the original weight of the flask, which gives the true weight of the glass. The weight of the glass is next subtracted from the weight of the flask and contained vapour (now condensed), which gives the weight of material used in the experiment. The volume which this weight of material occupied at the time of experiment is next corrected for temperature (to 0° C.) and pressure (760 millimetres) in the manner just described. The weight of a similar volume of hydrogen is next found.[†] The weights of equal volumes of hydrogen and vapour being thus determined, the density of the vapour, as compared with that of hydrogen = 1, is easily calculated. This process of finding the weight of a given volume of vapour was introduced by Dumas. Gay-Lussac's method consists in determining the volume of a given weight: it has been improved by Hofmann. An easy and excellent method by V. and C. Meyer consists, like that of Gay-Lussac, in determining the volume of the vapour of a given weight of a fluid or solid, but differs from it in so far that the volume of the vapour is ascertained by measuring an equal volume of air which the vapour is made to displace.

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* In France the conventional standard height of the barometer is 760 millimetres at 0° C. (32° F.); in Britain it is 30 inches, the temperature being 60° F. 760 millimetres is equivalent to 29·92 inches; but the expansion of the metal between 32° F. and 60° F. increases the length of the column to 30·005 inches. The standards are therefore almost identical.

† Corrected for the difference between the mercurial and air-thermometers, the coefficient of expansion of air is 0·003656 (Miller). The coefficient of expansion of different gases varies very slightly being somewhat higher for the more liquefiable gases.

As this method is the one which is now most commonly employed a somewhat detailed description of it may be given here.

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[*] 1 cubic centimetre of air at 0° C. and 760 millimetres weighs 0·001293 gramme.

[†] 1 litre (1000 cubic centimetres) of hydrogen at 0° C. and 760 millimetres (the barometer being at 0° C.) weighs 0·09 gramme. 100 cubic inches of hydrogen at 32° F. weigh 2·265 grains; at 60° F. 2·143 grains (the barometer being 30 inches at 60° F. in both cases). 100 cubic inches of air at 32° F. weigh 32·698 grains; at 60° F., 30·935 (barom. 30 inches at 60° F.). 1 cubic inch of water weighs 252·458 grains (Chaney, 252·279) at 62° F., and 30 inches. 1 gallon of water contains 277¼ (277·274 at 62° F.) cubic inches. 1 cubic foot contains about 6¼ gallons.

Vapour-density Determination by Meyer's Method.—The special form of apparatus employed is represented in fig. 46, and consists essentially of the three following parts:—1. The inner vessel *a*, which is really a flask having an elongated body, a very long narrow neck, and a nearly capillary side delivery-tube *b*; 2. The outer jacketing vessel *f*, which also is a flask of special shape; and 3. The measuring apparatus. In order to carry out a vapour-density determination, a suitable liquid, of boiling-point considerably higher than that of the substance under examination, is placed in the outer vessel and is there heated until it is in brisk ebullition and its vapour is condensing close to the top of the vessel. By this means the greater part of the inner vessel is surrounded by a jacket of hot vapour and is thereby raised to a practically uniform temperature. Prior to this preliminary heating operation, the outlet end of the delivery-tube *b* has been placed beneath the water in the vessel *d*, and, owing to the expansion of the air enclosed in *a*, bubbles make their escape at the surface of the water. During the heating, a weighed quantity of the substance to be examined (contained in a very small stoppered bulb) is suspended in the widened upper portion of the inner vsesel, just below the stopper *c* which, when replaced, closes the mouth of the vessel. As soon as bubbles no longer escape from *b*, the apparatus is ready for an experiment. The tube *e*, previously filled with water, is next inverted over the outlet end of *b* and then, by aid of a wire which passes, air-tight, through the stopper *c*, the bulb containing the substance is released, and falls to *g*, where a thin layer of asbestos has previously been placed

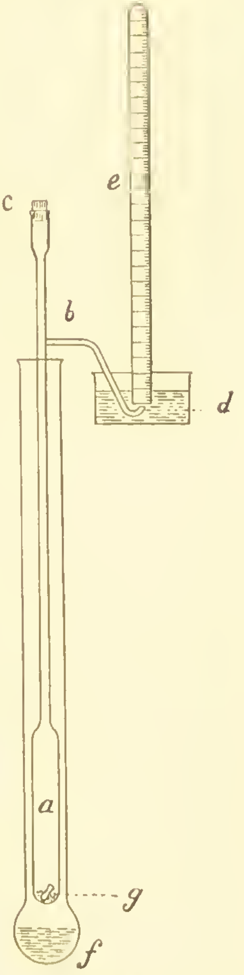

Fig. 46.—Meyer's Vapour-Density Apparatus.

to prevent its cracking the glass of the inner vessel. As a result of the high temperature at *g*, the stopper of the bulb is forced out and the whole of the liquid gradually becomes converted into vapour (which should not more than half fill the lower part of *a*). This vapour drives out of *a*, and into the measuring-tube, a quantity of air equal in volume to that which it itself occupies.

At the close of the experiment, the volume of the air in the measuring-tube is read off and reduced to standard temperature and pressure. The corrected volume represents, theoretically, the space which the weighed quantity of substance would occupy if it existed as vapour under normal conditions of temperature and pressure. From the results thus obtained, a simple calculation gives the vapour-density.

Determinations of the specific gravities or relative densities of gases, and of the vapour-densities of liquids (or of vaporizable solids), are carried out for the purpose of fixing the molecular weights of these various substances in the state of gas or vapour, and of assigning to them molecular formulæ. As already explained in the Section on the General Principles of Chemical Philosophy, the relative molecular weights of substances in the gaseous state are proportional to their relative densities (*see* pp. 46, 47). The molecular weight of hydrogen is chosen = 2 as standard for the comparison of the molecular weights of other substances in the gaseous state; but since the relative molecular weight and the relative density of each substance are proportional to each other, it follows that the number representing any molecular weight, in terms of the standard just mentioned (hydrogen = 2), may be obtained by doubling the number representing the relative density. The molecular weight of a substance thus having been ascertained, and the quantitative composition and empirical formula also having been determined (*see* p. 54), the molecular formula can be assigned. The quantitative value of any molecular formula must agree with the experimentally determined molecular weight of the substance which it purports to represent. Thus the determination of the quantitative composition of benzene and the necessary calculation lead to the empirical formula CH. But this formula would represent a substance of molecular weight 12·91, or of density (as vapour) $\frac{12{\cdot}91}{2} = 6{\cdot}455$, whereas the molecular weight of benzene as ascertained by doubling its vapour density is 77·46 (*i.e.*, 38·73 × 2). The only formula which corresponds to this molecular weight, as deduced from the vapour-density, is C_6H_6, and this, accordingly, is assumed as the molecular formula for benzene.

QUESTIONS AND EXERCISES

What is meant by the specific gravity or relative density of a substance?—In speaking of light and heavy bodies specifically, what standard of comparison is conventionally employed?—How are specific gravities expressed in figures?—Why should specific gravities be taken at one constant temperature?—How does the buoyancy of air affect the apparent weight of any material as ascertained by aid of the balance?—Give a direct method for taking the specific gravities of liquids.—A certain bottle holds 150 parts, by weight, of water, or 135·7 of diluted alcohol; show that the specific gravity of the latter is 0·9046.—An imperial fluid ounce of a liquid weighs 366½ grains; prove that its specific gravity is 0·838.—Equal volumes of benzol and glycerin weigh 34 and 49 grammes respectively, and the specific gravity of the benzol is 0·850; show that the specific gravity of the glycerin is 1·225.—Explain the process employed in taking the specific gravities of solid substances in mass and in powder.—State the method by which the specific gravity of a light body, such as cork, is obtained.—What modifications of the usual method are necessary in ascertaining the specific gravities of substances soluble in water?—How are the specific gravities of gases determined?—What are vapour-densities?—Describe Meyer's vapour-density apparatus.—By what law can the volume of a gas, at any required pressure, be deduced from its observed volume at another pressure?—To what extent will 78 volumes of a gas at 29·3 inches barometric pressure alter in volume when the pressure is 30·2 inches?—Write a short account of the means by which the volumes of gases are corrected for temperature.—At the temperature of 15° C. 40 litres of a gas are measured. To what volume will this gas contract on being cooled to the freezing-point of water (0° C.)? *Answer*, 37·916 litres.

Memorandum.—The next subjects of experimental study will be determined by the nature of the student's future pursuits. In most cases the operations of quantitative analysis will engage attention. These should include both volumetric and gravimetric determinations; and some details concerning both of these modes of making determinations are given in the following pages.

QUANTITATIVE ANALYSIS

INTRODUCTORY REMARKS

General Principles.—The proportions in which chemical substances unite with each other in forming compounds are definite and invariable (p. 42). Quantitative analysis is based on this law. When, for example, aqueous solutions of a silver salt and a chloride are mixed, a white curdy precipitate is produced containing chlorine and silver in atomic proportions —that is, 35·19 parts of chlorine to 107·11 of silver. No matter what the chloride or what the silver salt, the resulting silver chloride is invariable in composition. The formula AgCl is a convenient symbolic representation of this compound in these proportions. In the case of any known weight of a compound, of which the quantitative composition has been determined previously, the quantities of its constituents can be ascertained by simple calculation. Suppose, for instance, 8·53 parts of silver chloride have been obtained in some analytical operation: this quantity will be found by calculation to contain 2·109 parts of chlorine and 6·421 of silver. For if 142·3 (the formula weight) of silver chloride contain 35·19 (the atomic weight) of chlorine, 8·53 of silver chloride will contain $\frac{35{\cdot}19 \times 8{\cdot}53}{142{\cdot}3} = 2{\cdot}109$ of chlorine; and if 142·3 of silver chloride contain 107·11 of silver, 8·53 of silver chloride will contain $\frac{107{\cdot}11 \times 8{\cdot}53}{142{\cdot}3} = 6{\cdot}421$ of silver. To ascertain, for example, the quantity of silver in a substance containing, say, silver nitrate, all that is necessary is to take a weighed quantity of the substance, dissolve it, precipitate the whole of the silver by adding hydrochloric acid or other soluble chloride until silver chloride is no longer produced, collect the precipitate on a filter, wash, dry, and weigh. The quantity of silver in the dried chloride, ascertained by calculation, is the quantity of silver in the weighed portion of substance on which the operation was conducted; a further simple calculation gives the quantity per cent.—the form in which the results of quantitative analysis are usually stated. Occasionally a constituent of a substance admits of being isolated and weighed in the uncombined state. Thus the quantity of mercury in a substance may be determined by separating and weighing the mercury in the metallic condition; if the substance under examination be calomel (HgCl) or corrosive sublimate ($HgCl_2$), the proportion of chlorine may then be ascertained by calculation (Hg = 198·8; Cl = 35·19), or a chlorine determination may be made.

Nature of Gravimetric Quantitative Analysis.—As stated above, an element may sometimes be isolated and *weighed* and its quantity thus ascertained; or it may be separated and weighed in combination with another element whose combining proportion is well known; this is quantitative analysis by the *gravimetric* method.

Nature of Volumetric Quantitative Analysis.—Volumetric operations depend for success on some accurate initial gravimetric operation. A *weighed* quantity of a pure salt is dissolved in water or other fluid, and the solution is made up to a definite *volume* so as to obtain a *standard solution*. Quantitative analysis by the *volumetric* method consists in ascertaining the volume of the standard liquid which must be added to the substance under examination before a given effect is produced. Thus, for instance, a solution of silver nitrate of known strength may be used in experimentally determining an unknown quantity of a chloride in any substance. The silver solution is added to a solution of a definite quantity of the substance until flocks of silver chloride are no longer precipitated: every 107·11 parts of silver added (or 168·69 of silver nitrate) indicate the presence of 35·19 of chlorine, or an equivalent quantity of any chloride. The preparation of a standard solution, such as that of the silver nitrate to which allusion is here made, requires much care; but once it is prepared, certain analyses can, as already indicated, be executed with far greater rapidity and ease than by gravimetric processes.

In the following pages an outline of volumetric and gravimetric quantitative analysis is given. The scope of this work precludes any attempt to describe all the little mechanical details observed by quantitative analysts; essential operations, however, are so fully treated that careful manipulators will meet with little difficulty.

VOLUMETRIC ANALYSIS

Preliminary Note.—Great care should be observed in selecting a *fair* sample of any bulk of material that is to be examined either by volumetric or gravimetric analysis. If the whole quantity is in separate parcels, and if there is any ground for believing that the parcels differ in quality, they should, if practicable, be carefully mixed, or, technically, "bulked." Small portions should be taken from different parts of the resulting heap and well mixed in a mortar or other vessel, or, in certain cases, dissolved, and the solution well stirred or shaken. A specimen of the powder, or a portion of the solution, may then be selected for analysis.

Introduction.—The operations of volumetric analysis consist (*a*) in carrying out some definite *chemical reaction*, already well known to the operator, with (*b*) *definite quantities* of substances or salts; (*c*) the exact termination of the reaction between the two salts or substances being ascertained—usually by some *chemical indicator* (litmus, starch, etc.). A portion of the substance to be tested is carefully weighed and dissolved. To this solution there is gradually added the second substance contained in the testing fluid, commonly termed the Standard Volumetric Solution. The usefulness, and indeed the preparation, of this Standard Solution is founded (as already indicated on page 711) on some accurate initial gravimetric operation. A *weighed* quantity of a pure salt is dissolved in water, and the solution is made up to a definite volume so as to obtain a Standard Volumetric Solution. Accurately *measured* volumes of such a Standard Volumetric Solution will obviously contain just as definite quantities of the dissolved salt as if those quantities were *weighed* in a balance; and as measuring occupies less time than weighing, the volumetric operations can be conducted with great economy of time as compared with the corresponding gravimetric operations. A *standard solution* is one containing a known quantity of substance in unit volume.

A normal solution is a solution one litre of which represents, more or less directly, the chemical value or activity of the atomic weight of hydrogen taken in grammes (H = 1, that is, 1 gramme). A *decinormal solution* is one-tenth the strength of a normal solution. *A centinormal solution* is one-hundredth the strength of a normal solution. The normal solution of iodine (H = 1, I = 125·9) would contain 125·9 grammes of iodine per litre; that quantity being capable of displacing, or otherwise being equal in chemical activity to, 1 gramme of hydrogen. The official Volumetric Solution of Iodine containing 12·59 grammes per litre, is a decinormal solution. The official Volumetric Solution of Silver Nitrate containing 16·869 grammes of the salt in one litre ($AgNO_3$ = 168·69 ÷ 10), is a decinormal solution. The official Volumetric Solutions of Soda (NaOH = 39·76 grammes per litre), and Sulphuric Acid (H_2SO_4 = 97·34 ÷ 2, that is, 48·67 grammes per litre), are normal solutions. Solutions of hydrochloric acid containing 36·19 grammes of hydrogen chloride (HCl = 36·19) per litre; of oxalic acid containing 62·55 grammes of crystallized oxalic acid ($H_2C_2O_4$, $2H_2O$ = 125·10 ÷ 2) per litre; and of phosphoric acid containing 32·44 grammes of hydrogen phosphate (H_3PO_4 = 97·32 ÷ 3) per litre, would be normal solutions. The molecule of potassium bichromate ($K_2Cr_2O_7$ = 292·3) in presence of an acid, yields three atoms of oxygen available for direct oxidation, or for union with six atoms of hydrogen, therefore a solution of 48·71 grammes (292·3 ÷ 6) per litre would be a normal solution. The official Volumetric Solution of Potassium Bichromate contains one-tenth of this quantity, and is, therefore, a decinormal solution. The official Volumetric Solution of Sodium Thiosulphate is decinormal, for the molecular weight in grammes ($Na_2S_2O_3$, $5H_2O$ = 246·44) loses one atomic weight of sodium in grammes (Na = 22·88) when attacked by one atomic weight of iodine in grammes (I = 125·9), a quantity equal in chemical value or activity to the atomic weight of hydrogen in grammes (H = 1); and as the official Thiosulphate Solution, like the official Iodine Solution, contains only one-tenth of that hydrogen equivalent in grammes, it is a decinormal solution.

Apparatus

The only special vessels necessary in volumetric quantitative operations are:—1. A *one-litre flask* (fig. 47) which, when filled to a mark on the neck, contains, at 15·5° C., or 60° F., one litre (1000 cubic centimetres, or, rather, 1000 grammes of water*); it serves for preparing solutions in quantities of one litre. 2. A tall cylindrical *graduated jar* (fig. 48) which, filled to the highest graduation, contains 1000 grammes of distilled water at 60° F. (15·5° C.), divided into 100 equal parts; it serves for the measurement and admixture of decimal or centesimal parts of the litre. 3. A graduated tube or *burette* (fig. 49), the marked portion of which, when filled to "0," holds 100 grammes of distilled water, and is divided into 100 equal parts, or 50 grammes and divided into 50 equal parts, each of which is taken as corresponding to 1 cubic centimetre, with subdivisions, each subdivision being further subdivided; it is used for accurately measuring small volumes of liquids. A stopcock is fitted to the contracted portion, or other modes of arresting the flow of liquid may be adopted.

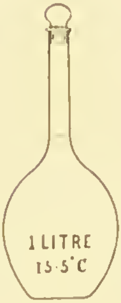

FIG. 47.—A Litre Flask.

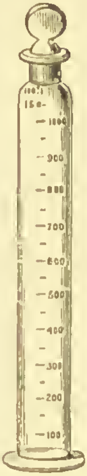

FIG. 48.—A Litre Jar.

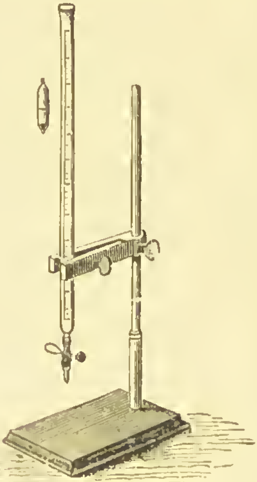

FIG. 49.—A Burette, etc.

The accurate reading of the height of a solution in the burette is a matter of great importance; it should be taken from the bottom of the curved surface, or *meniscus*, of the liquid. When reading the burette, the eye should be on the same level as the bottom of the meniscus. In the case of a coloured solution, when the bottom of the meniscus cannot be clearly seen, the reading must be taken from the surface of the liquid.

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* A cubic centimetre is the volume occupied by one gramme of distilled water at its point of greatest density, namely, 4° C. Metric measurements, however, are officially taken at 15·5° C. (60° F.).

Occasionally a hollow glass float or bulb (Erdmann's float, *see* fig. 49) is employed, of such a width that it can move freely in the tube without undue friction, and so adjusted in weight that it shall sink to more than half its length in any ordinary liquid. A fine line is scratched round the centre of the float; this line must always be regarded as marking the height of the fluid in the burette. In charging the burette, a solution is poured in, not until its surface is coincident with 0, but until the mark on the float is coincident with 0.

DETERMINATION OF ALKALIES

Volumetric Solution of Sulphuric Acid

(Sulphuric Acid, $H_2SO_4 = 97{\cdot}34$.)

The sulphuric radical, being bivalent, and most of the metals contained in the salts which are determined by means of standard sulphuric acid solution being univalent, it is convenient that each litre of this solution should contain half a molecular weight (the hydrogen equivalent), in grammes, of the acid ($H_2SO_4 = 97{\cdot}34$, and $97{\cdot}34 \div 2 = 48{\cdot}67$). A solution of this strength is a normal solution.

As it is not always easy to obtain pure sulphuric acid, the solution may be made from the commercial acid by mixing 50 grammes with five or six times its volume of water and after cooling adding sufficient water to make a litre of solution. The exact quantity of acid present in this solution may then be determined by titration with pure sodium carbonate, making use of the following memoranda:—

$$\underbrace{Na_2CO_3}_{\substack{2)105{\cdot}31 \\ \overline{52{\cdot}655}}} + \underbrace{H_2SO_4}_{\substack{2)97{\cdot}34 \\ \overline{48{\cdot}67}}} = Na_2SO_4 + CO_2 + H_2O$$

Pure anhydrous sodium carbonate can be prepared readily, for commercial bicarbonate is usually of such purity that when a small quantity is heated to redness for a quarter of an hour, the resulting carbonate is practically free from impurity. The bicarbonate should, however, be tested, and if more than traces of chlorides and sulphates are present, these may be removed by washing a few hundred grammes, first with a saturated solution of sodium bicarbonate, and afterwards with pure distilled water. After drying, the salt is ready for ignition—a few grammes in a small crucible.

About half a gramme of the sodium carbonate is accurately weighed and placed in a half-pint flask, around the neck of which twine has been wound to protect the fingers when the heated vessel is shaken by the operator (page 122). The salt is dissolved in water to about one-third the capacity of the flask, and a few drops of the indicator, blue solution of litmus, are added. The acid solution to be "set" or "standardized" is then poured into a burette and run therefrom into the flask until the reddened litmus indicates the presence of free acid. This will be due in the first place to carbonic acid liberated and remaining dissolved in the solution; hence the contents of the flask must be gently boiled for several minutes to expel carbonic anhydride, when the blue colour will have returned. More acid is then run in until the mixture, after boiling, remains of a neutral colour, indicating that just enough acid has been added to complete the reaction expressed in the foregoing equation.

Let it be supposed that 0·6 gramme of sodium carbonate was taken, and that this required 11 c.c. of sulphuric acid solution, how many c.c. of this solution would contain 48·67 grammes of pure sulphuric acid; or, what is equivalent in the reaction, how many c.c. would be required to neutralize 52·65 grammes of sodium carbonate? By rule of three, $0·6 : 11 :: 52·65 : x$, and $x = 965·25$; therefore in the example taken 965·25 c.c. are equivalent to 52·65 grammes of sodium carbonate, and contain 48·67 grammes of sulphuric acid.

This solution may be diluted with water, every 965·25 c.c. to be diluted to 1000 c.c., so that 1000 c.c. shall contain 48·67 grammes of sulphuric acid, or it may be used as it is and the necessary correction applied.

Borax, purified by recrystallization, is recommended by Rimbach for standardizing acids, in place of sodium carbonate. When it is used, the indicator employed should be methyl orange, which is not affected by boric acid.

The following substances may be tested conveniently by means of the standard solution of sulphuric acid:—

Solutions of Ammonia.—Two or three grammes of dilute, or about 1 gramme of strong solution of ammonia, are convenient quantities to operate upon. The weighing is most conveniently accomplished by taking a small stoppered bottle containing half an ounce or so of the substance, and having ascertained its total weight, transferring about the quantity desired to the flask in which the estimation is to be conducted, and again weighing the bottle with what remains in it. The difference is the exact quantity taken. The weighing of the ammonia solution having been accomplished, water is added, to about one-third the capacity of the flask (or, better, the ammonia is added to water already in the flask), and a few drops of solution of litmus are introduced. The titration is then conducted as described before, except that no heat is employed.

$$\underbrace{2NH_4OH}_{\begin{array}{c}2)69\cdot64\\ \hline 34\cdot82\end{array}} + \underbrace{H_2SO_4}_{\begin{array}{c}2)97\cdot34\\ \hline 48\cdot67\end{array}} = (NH_4)_2SO_4 + 2H_2O \qquad \text{= grammes in 1000 c.c. of normal solution.}$$

$$\underbrace{2NH_3}_{\begin{array}{c}2)33\cdot88\\ \hline 16\cdot94\end{array}} + \underbrace{H_2SO_4}_{\begin{array}{c}2)97\cdot34\\ \hline 48\cdot67\end{array}} = (NH_4)_2SO_4 \qquad \text{= grammes in 1000 c.c. of normal solution.}$$

1000 c.c. of normal solution, or its equivalent of a solution of any other concentration, would, according to this equation, neutralize 16·94 grammes of ammonia gas (NH_3) or 34·82 grammes of ammonium hydroxide (NH_4OH). If 3 grammes of ammonia solution had been taken, and it had required 15 c.c. of normal sulphuric acid solution, then the quantity of ammonia gas or ammonium hydroxide it contained would be seen by the following calculations:—

1000 c.c. : 16·94 g. NH_3 :: 15 c.c. : x = ·254 grammes NH_3
1000 c.c. : 34·82 g. NH_4OH :: 15 c.c. : x = ·522 grammes NH_4OH

Three grammes, then, would contain ·254 grammes of the gas, or ·522 grammes of ammonium hydroxide. Or in percentages:—

3 g. sol. : ·254 g. NH_3 :: 100 g. sol. : x g. NH_3 = 8·47 % NH_3
3 g. sol. : ·522 g. NH_4OH :: 100 g. sol. : x g. NH_4HO = 17·4 % NH_4OH

The solution would therefore contain 8·47 per cent. of ammonia gas (NH_3) or 17·4 per cent. of ammonium hydroxide

(NH_4OH). If the sulphuric acid solution was not of full standard, the number of c.c. which contained 48·67 grammes of sulphuric acid, which was, in fact, equivalent to 1000 c.c. of normal solution, might be substituted for 1000 c.c. in the preceding calculations.

A comparison should now be made with the requirements of the Pharmacopœia. It is useful to express results as percentage of substance of pharmacopœial strength in the material examined. Thus the British Pharmacopœia requires dilute ammonia solution to contain 10 per cent. by weight of the gas (NH_3). The solution supposed to have been operated on contained 8·47 per cent. NH_3, therefore it contains 84·7 per cent. of the dilute ammonia of the British Pharmacopœia.*

Strong Solution of Ammonia, B.P., contains 32·5 per cent. by weight of ammonia gas (NH_3).

Note.—The calculations just described for ammonia are similar to those employed throughout volumetric analysis; they will not be repeated, therefore, in the case of every substance.

"*Ammonium Carbonate.*"—The reaction indicated by the

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* Extremely minute quantities of ammonia—1 part in many millions of water—may be determined volumetrically by adding excess of a colourless, strongly alkaline, solution of mercuric iodide and potassium iodide, "Solution of Potassio-mercuric Iodide," B.P., or "Nessler's Reagent"; then in a similar vessel, containing an equal amount of pure water with excess of the Nessler reagent, imitating the depth of yellow or reddish-yellow colour thus produced by adding a solution containing a known quantity of an ammonium salt. The quantity of ammonia thus added represents the quantity in the original liquid.

The Nessler Reagent.—A litre may be made by dissolving 30 or 40 grammes of potassium iodide in a small quantity of hot water, adding a hot concentrated solution of mercuric chloride until the precipitate of mercuric iodide ceases to redissolve even by the aid of rapid stirring and heat, slightly diluting, filtering, adding a concentrated solution of (120 to 140 grammes of) caustic soda, or (160 to 180 grammes of) caustic potash, and diluting to one litre. A few c.c. (5 or 6 or more) of a concentrated solution of mercuric chloride are finally stirred in, the whole set aside till all precipitated mercuric iodide has deposited, and the clear liquid is then decanted for use. The reaction of this Nessler test with ammonia is as follows:—

$$NH_3 + 2HgI_2 + 3KOH = NHg_2I + 3KI + 3H_2O$$

Potassio-mercuric Iodide, without alkali, is commonly known as *Mayer's Reagent*, $KHgI_3$. A decinormal solution is a convenient one to use.

following equation occurs between commercial ammonium carbonate and sulphuric acid:—

$$\underbrace{2N_3H_{11}C_2O_5}_{6)312{\cdot}08} + \underbrace{3H_2SO_4}_{6)292{\cdot}02} = 3(NH_4)_2SO_4 + 2H_2O = 4CO_2$$

$$\overline{52{\cdot}01} \qquad \overline{48{\cdot}67} = \text{grammes in 1000 c.c. of normal solution.}$$

About 1 gramme is a convenient quantity to operate upon. Solution of litmus is the indicator, and the titration is conducted at a temperature just short of boiling. The determination is not very satisfactory, because the heat employed, while scarcely sufficient to expel the carbonic anhydride, is enough to occasion loss of ammonium salt. To avoid error, add excess of the normal acid solution and thus fix every trace of ammonia; then gently boil to get rid of carbonic anhydride; bring back the liquid to neutrality by an observed volume of normal alkaline solution, and deduct an equivalent volume of acid from the quantity first added.

Spiritus Ammoniæ Aromaticus, B.P.—The *alkalinity* of the official sal volatile (*see* p. 99) should be such that "20 cubic centimetres require for neutralization 25·5 cubic centimetres of the volumetric solution of sulphuric acid"; and, if the proper proportion of ammonium *carbonate* is present, "20 cubic centimetres, after the addition of 16 cubic centimetres of solution of barium chloride, should yield a precipitate which becomes more copious on heating to 160° F. (71° C.), and after filtering, the filtrate should yield a further precipitate when more of the reagent is added and the liquid is again heated."

Borax.—Two or three grammes is a convenient quantity.

$$\underbrace{Na_2B_4O_7,10H_2O}_{2)379{\cdot}12} + \underbrace{H_2SO_4}_{2)97{\cdot}34} = Na_2SO_4 + 4H_3BO_3 + 5H_2O$$

$$\overline{189{\cdot}56} \qquad \overline{48{\cdot}67} = \text{grammes in 1000 c.c. of normal solution.}$$

Solution of litmus is the indicator, and the titration may be carried on without heat. The liberation of boric acid colours the litmus wine-red. This is not regarded, the titration being continued until the bright red due to the action of free sulphuric acid makes its appearance. Methyl orange may be used as the indicator, as it is not affected by boric acid. The British Pharmacopœia requires Borax to be pure.

Lime Water, and *Saccharated Solution of Lime.*—Measure about half a litre of lime water, or weigh about 25 grammes of the saccharated solution. The following equations give quantitative expressions of the reactions:—

$$\underbrace{\mathrm{Ca(OH)_2}}_{2)73\cdot47} + \underbrace{\mathrm{H_2SO_4}}_{2)97\cdot34} = \mathrm{CaSO_4} + 2\mathrm{H_2O}$$

$$\overline{\quad 36\cdot735 \quad} \qquad \overline{\quad 48\cdot67 \quad} = \text{grammes in 1000 c.c. of normal solution.}$$

Or,

$$\underbrace{\mathrm{CaO}}_{2)55\cdot59} + \underbrace{\mathrm{H_2SO_4}}_{2)97\cdot34} = \mathrm{CaSO_4} + \mathrm{H_2O}$$

$$\overline{\quad 27\cdot795 \quad} \qquad \overline{\quad 48\cdot67 \quad} = \text{grammes in 1000 c.c. of normal solution.}$$

Litmus is used as an indicator. One litre of Lime Water, B.P., contains about 1·5 gramme of calcium hydroxide, $\mathrm{Ca(OH)_2}$, equal to about 1·2 gramme of quicklime, CaO. Ten fluid ounces contain $6\frac{2}{3}$ grains of calcium hydroxide.

Sodium. Caustic Potash and Soda. Potassium and Sodium Carbonates and Bicarbonates.—Litmus is the indicator throughout, and heat is used in all cases, for the caustic alkalies always contain some carbonate.

$$\underbrace{2\mathrm{Na}}_{2)45\cdot76} + \underbrace{\mathrm{H_2SO_4}}_{2)97\cdot34} = \mathrm{H_2} + \mathrm{Na_2SO_4}$$

$$\overline{\quad 22\cdot88 \quad} \qquad \overline{\quad 48\cdot67 \quad} = \text{grammes in 1000 c.c. of normal solution.}$$

$$\underbrace{2\mathrm{KOH}}_{2)111\cdot42} + \underbrace{\mathrm{H_2SO_4}}_{2)97\cdot34} = \mathrm{K_2SO_4} + 2\mathrm{H_2O}$$

$$\overline{\quad 55\cdot71 \quad} \qquad \overline{\quad 48\cdot67 \quad} = \text{grammes in 1000 c.c. of normal solution.}$$

$$\underbrace{2\mathrm{NaOH}}_{2)79\cdot52} + \underbrace{\mathrm{H_2SO_4}}_{2)97\cdot34} = \mathrm{Na_2SO_4} + 2\mathrm{H_2O}$$

$$\overline{\quad 39\cdot76 \quad} \qquad \overline{\quad 48\cdot67 \quad} = \text{grammes in 1000 c.c. of normal solution.}$$

$$\underbrace{\mathrm{K_2CO_3}}_{2)137\cdot21} + \underbrace{\mathrm{H_2SO_4}}_{2)97\cdot34} + = \mathrm{K_2SO_4} + \mathrm{CO_2} + \mathrm{H_2O}$$

$$\overline{\quad 68\cdot605 \quad} \qquad \overline{\quad 48\cdot67 \quad} = \text{grammes in 1000 c.c. of normal solution.}$$

$$\text{Or, } \underbrace{K_2CO_3 + 16\%\text{ Water}}_{\substack{2)163\cdot34 \\ \overline{81\cdot67}}} + \underbrace{H_2SO_4}_{\substack{2)97\cdot34 \\ \overline{48\cdot67}}} = K_2SO_4 + CO_2 + xH_2O$$

{ = grammes in 1000 c.c. of normal solution.

$$\underbrace{Na_2CO_3}_{\substack{2)105\cdot31 \\ \overline{52\cdot655}}} + \underbrace{H_2SO_4}_{\substack{2)97\cdot34 \\ \overline{48\cdot67}}} = Na_2SO_4 + CO_2 + H_2O$$

= grammes in 1000 c.c. of normal solution.

$$\text{Or, } \underbrace{Na_2CO_3,10H_2O}_{\substack{2)284\cdot11 \\ \overline{142\cdot055}}} + \underbrace{H_2SO_4}_{\substack{2)97\cdot34 \\ \overline{48\cdot67}}} = Na_2SO_4 + CO_2 + 11H_2O$$

= grammes in 1000 c.c. of normal solution.

$$\underbrace{2KHCO_3}_{\substack{2)198\cdot76 \\ \overline{99\cdot38}}} + \underbrace{H_2SO_4}_{\substack{2)97\cdot34 \\ \overline{48\cdot67}}} = K_2SO_4 + 2CO_2 + 2H_2O$$

= grammes in 1000 c.c. of normal solution.

$$\underbrace{2NaHCO_3}_{\substack{2)166\cdot86 \\ \overline{83\cdot43}}} + \underbrace{H_2SO_4}_{\substack{2)97\cdot34 \\ \overline{48\cdot67}}} = Na_2SO_4 + 2CO_2 + 2H_2O$$

= grammes in 1000 c.c. of normal solution.

Convenient quantities to operate with are: of sodium, 0·4 or 0·5 gramme, placed on 10 or 20 c.c. of water in a basin, the latter being immediately covered with a glass plate to preserve the face and hands from any caustic spurtings and to prevent loss of soda; of caustic potash, 1 gramme; caustic soda, 0·5 to 1 gramme; potassium carbonate, or bicarbonate, 1 to 2 grammes; sodium carbonate, or bicarbonate, 2 to 3 grammes; dried sodium carbonate, 0·5 to 1 gramme; and of solutions a corresponding quantity.

Potassium and Sodium Tartrates and Citrates.—When alkali-metal tartrates or citrates are burned in the open air, the whole of the metal remains in the form of carbonate. Each formula weight of a normal tartrate gives one formula weight of carbonate, and twice the formula weight of an acid tartrate gives one formula weight of carbonate. Advantage is taken of these reactions to determine indirectly the quantity of citrate or tartrate in presence of substances with which they are generally associated. One or two grammes of any of these salts is a convenient quantity to operate upon. The ignition may be conducted in a platinum or porcelain crucible. A low red heat only should be used, and the vessel removed when complete carbonization has been effected—that is to say, when nothing remains but the carbonate and free carbon. The mixture is then treated with hot water, and the carbon separated by filtration. If too little heat has been used, and carbonization is not complete, the filtrate will be more or less coloured. If this should be the case, the operation must be repeated with a fresh quantity of material. The carbonate is titrated in the usual way. The following equations explain the reactions :—

$$\underbrace{(K_2C_4H_4O_6)_2,H_2O}_{\substack{4)467\cdot04 \\ \overline{116\cdot76}}} + 5O_2 = \underbrace{2K_2CO_3}_{\substack{4)274\cdot42 \\ \overline{68\cdot605}}} + 6CO_2 + 5H_2O \qquad 68\cdot605\left\{\begin{array}{l}\text{equiv. to 1000 c.c. of} \\ \text{normal sulphuric acid sol.}\end{array}\right.$$

$$\underbrace{2KHC_4H_4O_6}_{\substack{2)373\cdot5 \\ \overline{186\cdot75}}} + 5O_2 = \underbrace{K_2CO_3}_{\substack{2)137\cdot21 \\ \overline{68\cdot605}}} + 7CO_3 + 5H_2O \qquad 68\cdot605\left\{\begin{array}{l}\text{equiv. to 1000 c.c. of} \\ \text{normal sulphuric acid sol.}\end{array}\right.$$

$$\underbrace{2K_3C_6H_5O_7}_{\substack{6)608\cdot22 \\ \overline{101\cdot37}}} + 9O_2 = \underbrace{3K_2CO_3}_{\substack{6)411\cdot63 \\ \overline{68\cdot605}}} + 9CO_2 + 5H_2O \qquad 68\cdot605\left\{\begin{array}{l}\text{equiv. to 1000 c.c. of} \\ \text{normal sulphuric acid sol.}\end{array}\right.$$

$$\underbrace{2(KNaC_4H_4O_6,4H_2O)}_{\substack{4)560\cdot3 \\ \overline{140\cdot075}}} + 5O_2 = \underbrace{2KNaCO_3}_{\substack{4)242\cdot52 \\ \overline{60\cdot63}}} + 6CO_2 + 12H_2O \qquad 60\cdot63\left\{\begin{array}{l}\text{equiv. to 1000 c.c. of} \\ \text{normal sulphuric acid sol.}\end{array}\right.$$

It will be readily understood that in the first (for example) of the reactions just represented 116·76 parts by weight of potassium tartrate are equivalent to 68·6 of potassium carbonate; and as in a previous reaction it has been shown that 68·6 parts by weight of potassium carbonate are equivalent to 48·67 of sulphuric acid, it follows that 116·76 parts by weight of potassium tartrate are equivalent to 48·67 of sulphuric acid. Hence 116·76 grammes of potassium tartrate are equivalent to 48·67 grammes of sulphuric acid, or to 1000 c.c. of the standard solution of sulphuric acid. If the substance under examination be a crude sample of potassium tartrate, and if the number of c.c. of sulphuric acid used for 2 grammes of the sample has been 15 c.c., then as 1000 c.c. of the acid solution are equivalent to 116·76 grammes of potassium tartrate, 15 c.c. of the solution are equivalent to 1·75 gramme of potassium tartrate. As 2 grammes of the sample contain 1·75 of real potassium tartrate, the tartrate examined contains 87·5 per cent. of real tartrate. Commercial samples of this salt are practically pure as a rule. If calcium sulphate be present in such tartrates or citrates, loss of potassium carbonate will ensue, potassium sulphate being formed. In examining acid potassium tartrate, which is the salt most likely to contain calcium sulphate, direct titration with volumetric solution of sodium hydroxide may be employed (*see* next section). Seven or eight per cent. of calcium tartrate is commonly present in commercial cream of tartar. The British Pharmacopœia requires that the salt should not contain more than one-fortieth of impurities.——*Rochelle Salt* and *Sodium Benzoate* should each be pure within 1 per cent.

Notes.

Alkalimetry.—The foregoing processes are often spoken of as those of *alkalimetry* (the measurement of alkalies).

Neutral Solution of Litmus may be made by digesting the commercial fragments in about fifteen or twenty times their weight of water for a few hours, decanting, dividing into two equal portions, adding acid to one till it is faintly red, then pouring in the other and mixing. The solution may be kept in a stoppered bottle, and occasionally exposed to the air. It should never be filtered, but allowed gradually to deposit.

Weighing.—In the case of substances which are liable to alter by exposure to air, it is important that a selected quantity should be weighed, rather than that selected weights from the weight-box be accurately balanced by material, the former operation occupying much the shorter time. The procedure adopted for *Solutions of Ammonia* (p. 716) may also be employed.

QUESTIONS AND EXERCISES

On what fundamental laws are the operations of quantitative analysis based?—What is the general nature of *gravimetric* quantitative analysis?—Explain the principle of *volumetric* quantitative analysis.—Define (1) a *standard* and (2) a *normal* solution.—Describe the apparatus used in volumetric determinations. —One hundred cubic centimetres of solution of sulphuric acid contain 4·867 grammes of hydrogen sulphate; calculate what weights of potassium bicarbonate and anhydrous sodium carbonate that volume will neutralize. *Ans.*, 9·938 grammes and 5·2655 grammes.—Show what weight of potassium hydroxide is contained in a solution of potash 48·02 grammes of which are neutralized by 50 c.c. of normal solution of sulphuric acid. *Ans.*, 5·80 per cent.—Calculate the percentage of calcium hydroxide in lime water 480 grammes of which are neutralized by 20 c.c. of the volumetric solution of sulphuric acid. *Ans.*, 0·153. —Eight grammes of a sample of Rochelle salt, after ignition, etc., require 54·3 c.c. of the official sulphuric acid solution for complete neutralization; calculate the centesimal proportion of sodium potassium tartrate present. *Ans.*, 95·076.

DETERMINATION OF ACIDS

In the previous experiments a known quantity of an acid has been used in determining unknown quantities of alkalies. In those about to be described a known quantity of an alkali is employed in determining unknown quantities of acids. The alkali selected may be either a hydroxide or a carbonate, but the former is to be preferred; for the carbonic acid set free when a strong acid is added to a carbonate, interferes to some extent with the indications of alkalinity, acidity, or neutrality, afforded by litmus. The alkali most convenient for use is caustic soda, a solution of which has probably already been made the subject of experiment in operations with the normal solution of sulphuric acid. It should be kept in a stoppered bottle, and exposed to air as little as possible.

Volumetric Solution of Caustic Soda

(Sodium Hydroxide, $NaOH = 39·76$.)

This aqueous solution is most conveniently made of such concentration that 1000 c.c. contain one formula weight in grammes of the alkali ($NaOH = 39·76$). It will be seen from the following equation that 39·76 grammes of sodium hydroxide convert 48·67 grammes of sulphuric acid into neutral sodium sulphate. Therefore one litre of this normal solution, containing 39·76 grammes of caustic soda, will form a neutral solution of sulphate with one litre of normal sulphuric acid solution, or with a chemically equivalent quantity of sulphuric acid solution of any other concentration :—

$$\underbrace{H_2SO_4}_{2)97{\cdot}34} \quad + \quad \underbrace{2NaOH}_{2)79{\cdot}52} = Na_2SO_4 + 2H_2O$$

$\overline{48{\cdot}67}$ = 1000 c.c. of normal solution. $\overline{39{\cdot}76}$ = 1000 c.c. of normal solution.

If pure sodium hydroxide were at hand, it would only be necessary to weigh 39·76 grammes, dissolve this in water, and dilute to one litre. But the pure hydroxide cannot readily be obtained. Therefore weigh about 45 grammes of ordinary caustic soda, dissolve in water, and when cool make up the volume of the solution to one litre. Then take, say, 14 c.c., dilute with more water in a flask, add a few drops of solution of litmus, and titrate with sulphuric acid solution of known concentration. Suppose that the volume of normal acid solution required to neutralize the 14 c.c. of the soda solution has been 15 c.c., or that an equivalent quantity of acid solution of another concentration has been used ; then, how many c.c. of the soda solution are equivalent to 1000 c.c. of normal acid solution ; or, what comes to the same thing, how many c.c. of the solution contain 39·76 grammes of sodium hydroxide? It is found that 933 c.c. of the solution contain, 39·76 grammes of sodium hydroxide. The solution may either be diluted, every 933 c.c. to 1000 c.c., so that it may be normal (1000 c.c. = 39·76 grammes NaOH), or it may be used without dilution (933 c.c. = 39·76 grammes NaOH), care being taken to introduce the necessary correction. It has already been mentioned that caustic soda nearly always contains carbonate. To remove resulting carbonic acid, therefore, the solution should be heated towards the close of each titration in all the determinations in which litmus is the indicator. When methyl orange is used no boiling is required, as that indicator is not affected by carbonic acid. The following substances are among those which may be determined with normal sodium hydroxide solution.

Acetic Acid.—Operate upon about 1 gramme of glacial acid, about 20 grammes of diluted acid, or about 3 grammes of ordinary acetic acid.

$$\underbrace{HC_2H_3O_2}_{59{\cdot}58} + \underbrace{NaOH}_{39{\cdot}76 \text{ = 1000 c.c. normal solution.}} = NaC_2H_3O_2 + H_2O$$

Acetic Acid, B.P., should contain 33 per cent. of hydrogen acetate ($HC_2H_3O_2$). Diluted Acetic Acid, B.P., 4·27 per cent. Glacial Acetic Acid, B.P., 99 per cent.

Citric Acid.—Operate on about 1 gramme. The reaction is represented by the following equation :—

$$\underbrace{H_3C_6H_5O_7,H_2O}_{\substack{\underline{3)208\cdot5}\\ 69\cdot5}} + \underbrace{3NaOH}_{\substack{\underline{3)119\cdot28}\\ 39\cdot76 \text{ = 1000 c.c. normal solution.}}} = Na_3C_6H_5O_7 + 4H_2O$$

Hydrochloric Acid.—Operate on from 1 to 2 grammes of the concentrated acid, or on about 4 grammes of the diluted acid.

$$\underbrace{HCl}_{36\cdot19} + \underbrace{NaOH}_{39\cdot76 \text{ = 1000 c.c. normal solution.}} = NaCl + H_2O$$

Hydrochloric Acid, B.P., should contain 31·79 per cent. of real acid (HCl); and Diluted Hydrochloric Acid, B.P., 10·58 per cent. Diluted Hydrobromic Acid, 10 per cent. (HBr).

Lactic Acid, B.P., contains about 75 per cent. of real acid.

Nitric Acid.—Operate on from 1 to 2 grammes of concentrated, or on 4 to 5 grammes of diluted acid.

$$\underbrace{HNO_3}_{62\cdot58} + \underbrace{NaOH}_{39\cdot76 \text{ = grammes in 1000 c.c. normal solution.}} = NaNO_3 + H_2O$$

Nitric Acid, B.P., should contain 70 per cent.; and Diluted Nitric Acid, B.P., 17·44 per cent. of hydrogen nitrate (HNO_3).

Nitrohydrochloric Acid.—Operate upon 4 to 5 grammes of diluted acid. The reaction is a complex one. The British Pharmacopœia requires that 4 grammes of the diluted acid should neutralize about 10 c.c. of volumetric solution of sodium hydroxide.

Sulphuric Acid.—Operate upon from 0·5 to 1 gramme of concentrated acid, or from 4 to 5 grammes of either Diluted or Aromatic Sulphuric Acid.

$$\underbrace{H_2SO_4}_{\substack{\underline{2)97\cdot34}\\ 48\cdot67}} + \underbrace{2NaOH}_{\substack{\underline{2)79\cdot52}\\ 39\cdot76 \text{ = grammes in 1000 c.c. normal solution.}}} = Na_2SO_4 + 2H_2O$$

Sulphuric Acid, B.P., should contain 98 per cent.; Diluted, B.P., 13·65 per cent.; and Aromatic, B.P., the equivalent of 13·8 per cent. of hydrogen sulphate (H_2SO_4).

Tartaric Acid.—Operate upon about 1 gramme of the acid. The following equation represents the reaction :—

$$\underbrace{H_2C_4H_4O_6}_{\begin{array}{c}2)148{\cdot}92\\ \hline 74{\cdot}46\end{array}} + \underbrace{2NaOH}_{\begin{array}{c}2)79{\cdot}52\\ \hline 39{\cdot}76\end{array}} = Na_2C_4H_4O_6 + 2H_2O$$

= grammes in 1000 c.c. normal solution.

Notes.—1. Pure acetates, citrates more especially, tartrates, and some other organic salts, have an alkaline action on litmus, but not to an important extent. If the caustic soda solution be added to acetic, citric, or tartaric acid, containing litmus, until the liquid is fairly blue, the operator will obtain fairly trustworthy results; but in delicate experiments turmeric or phenol-phthalein should be used instead of litmus. Phenol-phthalein, B.P., is "produced by interaction of phenol and phthalic anhydride." Its tincture yields an intense red colour with caustic potash or soda, hence may be used as an indicator of the termination of volumetric reactions, especially those with organic acids. "Solution of Phenol-phthalein," B.P., is made by dissolving 0·4 gramme of phenol-phthalein in 200 c.c. of dilute alcohol.

2. The term *acidimetry* is applied to such operations as those described above for the determination of the quantities of acids in solutions.

QUESTIONS AND EXERCISES

Calculate the percentage of real acid present in dilute sulphuric acid 30 grammes of which are neutralized by 84 c.c. of the official volumetric solution of caustic soda. *Ans.*, 13·628.—Show how much real nitric acid is contained in a solution 36 grammes of which are neutralized by 94 c.c. of normal solution of sodium hydroxide. *Ans.*, 16·34 per cent.

DETERMINATION OF ACID RADICALS PRECIPITATED BY SILVER NITRATE

The purity of many salts and the concentrations of their solutions may be determined by this process; but officially it is chiefly used for the determination of diluted hydrocyanic acid, other cyanides, and some bromides and iodides.

STANDARD SOLUTION OF SILVER NITRATE

(Silver Nitrate, $AgNO_3 = 168\cdot69$.)

Dissolve 16·869 grammes of pure silver nitrate in one litre of water. 1000 c.c. of this solution contain $\frac{1}{10}$ of the formula weight in grammes of silver nitrate. It is therefore a decinormal solution.

If pure dry crystals of silver nitrate are not at disposal, and pure dry crystals of sodium chloride are at hand, a solution may be made of approximate strength and then be standardized by means of the latter salt. The method may be thus indicated :—

$$\underbrace{NaCl}_{10)58\cdot07} + \underbrace{AgNO_3}_{10)168\cdot69} = AgCl + NaNO_3$$

$$\overline{5\cdot807} \qquad \overline{16\cdot869}\left\{\begin{array}{l}= \text{grammes in 1000 c.c.}\\ \text{decinormal solution.}\end{array}\right.$$

Take rather less than 0·1 gramme of the sodium chloride (NaCl), and dissolve it in water. The silver chloride (AgCl) precipitated in the reaction is an insoluble salt, and the end of its precipitation will serve as a good indication of the completion of the reaction. A better indicator, however, is a drop of solution of potassium chromate; the potassium chromate used must be free from chloride. The silver nitrate does not act upon the chromate until all the chloride is converted into silver chloride, after which a deep red precipitate of silver chromate is produced. This indication is extremely delicate, and in practice is noticed when the white colour due to silver chloride changes to yellowish from formation of the first traces of silver chromate. Solutions should be cool and not very dilute.

Hydrocyanic Acid.—Three to four grammes of *diluted* acid form a convenient quantity to operate upon. The HCN is first converted into KCN or NaCN, with caustic potash or soda. The following equations explain the reactions :—

$$\underbrace{2HCN}_{10)53\cdot7} + 2NaOH = \underbrace{2NaCN}_{10)97\cdot46} + 2H_2O$$

$$\overline{5\cdot37} \qquad\qquad\qquad \overline{9\cdot746}$$

$$\underbrace{2NaCN}_{10)97\cdot46} + \underbrace{AgNO_3}_{10)168\cdot69} = NaCN,AgCN + NaNO_3$$

$$\overline{9\cdot746} \qquad \overline{16\cdot869} = \text{grammes in 1000 c.c. decinormal solution.}$$

It is seen that 5·37 grammes of hydrogen cyanide (HCN) are equivalent to 9·746 grammes of sodium cyanide, and represent 16·869 grammes of silver nitrate, or 1000 c.c. of decinormal solution of silver nitrate.

The sodium cyanide having been obtained, the titration is carried on until the salt is converted into the double salt (NaCN,AgCN), immediately after which a permanent turbidity occurs, due to precipitation of silver cyanide, thus:—

$$AgCN,NaCN + AgNO_3 = 2AgCN + NaNO_3$$

The commencement of this turbidity forms a delicate and satisfactory proof of the completion of the volumetric reaction.

There is, however, a difficulty in the conversion of the acid into the cyanide (Siebold), to which it is necessary to pay particular attention. Solution of litmus is added to the acid diluted largely with water, and the sodium hydroxide solution poured in. Owing to the strong alkaline reaction of the sodium cyanide formed, the mixture becomes blue when only a small proportion of the acid has been converted. If then the titration be conducted until the turbidity appears, only the sodium cyanide will be estimated, leaving free hydrocyanic acid still unacted upon. Indeed, sodium cyanide may be estimated in presence of hydrocyanic acid in this way. Thus the following reaction (expressed approximately) might occur:—

$$\underbrace{NaCN + 4HCN}_{\text{Alkaline.}} + AgNO_3 = \underbrace{AgCN + NaNO_3 + 4HCN}_{\text{Turbid and acid.}}$$

In this case only one-fifth of the cyanogen originally present would be precipitated. The mixture would, however, become acid. If this acidity be prevented, all difficulty is overcome. The following details (Senier) will be found to answer well. To the diluted hydrocyanic acid add caustic soda solution until a strongly alkaline reaction is shown by the solution of litmus. Then add the silver solution drop by drop from the burette, when in most cases the mixture will become acid. When it does so, add more soda solution, and repeat this process until the final reading, when the solution must be alkaline. In this way the addition of too much soda at the commencement, which would use up silver solution and make the reading a trifle too high, is avoided.

Diluted Hydrocyanic Acid, B.P. and U.S.P., should contain

2 per cent. of hydrogen cyanide (HCN); *Aqua Laurocerasi*, B.P., 0·1 per cent.

Potassium Cyanide.—A sample, of which 0·1 gramme, in *dilute* solution, requires 7·3 c.c. of decinormal silver nitrate solution, contains 95 per cent. of real cyanide. Any sulphide may be removed by shaking the solution with lead carbonate. Other ordinary impurities do not interfere.

The potassium cyanide of commerce very often contains considerable quantities of sodium cyanide. The cyanide in it is usually calculated to potassium cyanide, so that as the atomic weight of sodium is much less than that of potassium it is quite possible for a sample of "Potassium Cyanide" to appear as containing more than 100 per cent. of that salt.

Ammonium Bromide.—Take 0·1 to 0·2 gramme and conduct the titration in the same manner as for sodium chloride, using potassium chromate as indicator:—

$$\begin{array}{ccccccc} \underbrace{NH_4Br} & + & \underbrace{AgNO_3} & = & AgBr & + & NH_4NO_3 \\ 10)\overline{97{\cdot}29} & & 10)\overline{168{\cdot}69} & & & & \\ \overline{9{\cdot}729} & & \overline{16{\cdot}869} & \left\{ \begin{array}{l} = \text{grammes in 1000 c.c. of} \\ \quad \text{decinormal solution.} \end{array} \right. & & & \end{array}$$

Potassium Bromide.—Operate upon rather less than 0·1 gramme, and conduct the titration in the same manner as with sodium chloride, using potassium chromate as indicator:—

$$\begin{array}{ccccccc} \underbrace{KBr} & + & \underbrace{AgNO_3} & = & AgBr & + & KNO_3 \\ 10)\overline{118{\cdot}18} & & 10)\overline{168{\cdot}69} & & & & \\ \overline{11{\cdot}818} & & \overline{16{\cdot}869} & \left\{ \begin{array}{l} = \text{grammes in 1000 c.c. of} \\ \quad \text{decinormal solution.} \end{array} \right. & & & \end{array}$$

Remembering that 168·69 parts of silver nitrate ($AgNO_3 =$ 168·69) decompose 118·18 of potassium bromide ($KBr =$ 118·18), while on the one hand they decompose as little as 74·02 of potassium chloride ($KCl = 74{\cdot}02$), and on the other hand as much as 164·73 parts of potassium iodide ($KI =$ 164·73), it will be seen that the quantitative operation of the chloride as an impurity may neutralize the quantitative operation of the iodide. Hence the necessity to test the bromide qualitatively as well as quantitatively, and, as regards either impurity singly, of fixing maximum as well as minimum limits of the action of the volumetric solution of silver nitrate on potassium bromide. "Each gramme, dissolved in water, requires for complete precipitation not less than 83·7 nor more than 85·4 cubic centimetres of the volumetric solution of silver nitrate."

Potassium Iodide.—0·2 should require 12 c.c. The salt is often 98 or 99 per cent. pure, containing not more than 0·5 per cent. of chloride, a little sulphate and a little carbonate.

Sodium Iodide.—0·1 should require 6·65 c.c., equivalent to 99 per cent. of real iodide.

Potassium Iodide may be determined volumetrically by means of a twentieth normal solution of mercuric chloride, the termination of the operation being indicated by the commencement of the formation of a red precipitate :—

(1) $3KI + HgCl_2 = 2KCl + KHgI_3$ (soluble).
(2) $2KHgI_3 + HgCl_2 = 2KCl + 3HgI_2$ (insoluble).

The author of this process, M. Personné, stated in 1875 that neither chlorides, bromides, nor carbonates interfere. Carles dissolves the iodide in alcohol of 17½ per cent., as much excess of water may decompose the double iodide.

Ferrous Iodide.—Messrs Naylor and Hooper in 1881 demonstrated that Personne's solution is applicable to ferrous iodide, even in the state of syrup :—

(1) $2FeI_2 + HgCl_2 = FeCl_2 + FeI_2,HgI_2$ (soluble).
(2) $FeI_2,HgI_2 + HgCl_2 = FeCl_2 + 2HgI_2$ (insoluble).

The use of mercuric chloride for determining the strength of syrup of ferrous iodide was first suggested by E. Smith in 1859. The process was improved by T. & H. Smith in 1860.

Sodium Arsenate.—In the British Pharmacopœia of 1867, sodium arsenate was estimated by titration with standard solution of silver nitrate, a sufficient quantity of soda to convert it into tri-sodium arsenate being first added. The completion of the reaction was indicated by a precipitate no longer forming with more of the silver solution. As the termination of the reaction is ill-defined, and the amount of soda to be added can only be ascertained when the amount of arsenate is already known, this method is very unsatisfactory. The salt is now determined officially by precipitation with lead acetate. (*See* also pp. 734 and 738).

Spiritus Rectificatus, B.P., may contain traces of amyl alcohol and aldehyde; these may be detected by adding silver nitrate, which is reduced by them to the metallic state. Any quantity beyond a mere trace of such substances renders the alcohol too impure for use in medicine. "100 cubic centimetres, with 2 cubic centimetres of the volumetric solution of silver nitrate, exposed for twenty-four hours to bright light, and then decanted from the black powder which has formed, undergo no further change when again exposed to light with more of the volumetric solution."

QUESTIONS AND EXERCISES

Explain the volumetric method of determining the strength of aqueous solutions of hydrocyanic acid.—Calculate how much silver nitrate will indicate the presence of 1 part of real hydrocyanic acid. *Ans.*, 3·14 parts.

DETERMINATION OF SUBSTANCES READILY OXIDIZED

Any substance which quickly unites with a definite weight of oxygen, or is susceptible of any equivalent action, may be quantitatively tested by ascertaining how much of an oxidizing agent of known power must be added to a given quantity before complete oxidation is effected. The oxidizing agents employed for this purpose in the British Pharmacopœia are iodine and potassium bichromate. Potassium permanganate is often used for the same purpose. Iodine acts indirectly, by taking hydrogen from water and liberating oxygen; potassium bichromate directly, by the facility with which it yields three-sevenths of its oxygen—as indicated by the equations and statements given on pp. 736, 737; potassium permanganate, by affording five-eighths of its oxygen in presence of an acid, and an oxidizable substance (p. 740):—

$$2KMnO_4 + 4H_2SO_4 = 2KHSO_4 + 2MnSO_4 + 3H_2O + 5O$$

STANDARD SOLUTION OF IODINE

(Iodine, I = 125·9.)

If pure iodine be not at hand, it may be prepared by mixing the commercial article with about a fourth of its weight of potassium iodide and subliming. Sublimation may be effected by gently warming the mixture in a beaker, the mouth of which is closed by a funnel; the iodine vapour condenses on the funnel, while fixed impurities are left behind, and any chlorine which the iodine may contain is absorbed by the potassium iodide, an equivalent quantity of iodine being liberated. Small quantities may be similarly treated between two watch-glasses, placed edge to edge. Any trace of moisture in the resublimed iodine is removed by exposure "for a few hours under a glass shade placed over a dish containing concentrated sulphuric acid."

Place 12·59 grammes of pure iodine and about 18 grammes of pure potassium iodide (an aqueous solution of which is the best solvent of iodine; the salt plays no other part in these operations) in a litre flask, add a *little* water and agitate until the iodine is dissolved; dilute to 1 litre.

The following substances may be determined by this decinormal solution:—

Sulphurous Acid.—Operate on about 0·5 gramme of the acid, and dilute with water. If the sulphurous acid be diluted to a less degree than 0·04 or 0·05 per cent., there will be some risk of the sulphuric acid subsequently formed being again reduced to sulphurous acid, with liberation of iodine. In delicate experiments the distilled water used for dilution should previously be freed from air by boiling, to prevent the small amount of oxidizing action which dissolved air would exert. The solution of iodine is then added until a slight permanent brown tint is produced, showing the presence of free iodine. A better indicator of the termination of the reaction is starch mucilage, which gives a blue colour with the slightest trace of free iodine.

The following equation shows the reaction that takes place:—

$$\underbrace{H_2SO_3}_{20)81{\cdot}46} + H_2O + \underbrace{I_2}_{20)251{\cdot}8} = 2HI + H_2SO_4$$

$$\overline{\quad 4{\cdot}073 \quad} \qquad\qquad \overline{\quad 12{\cdot}59 \quad}\left\{\begin{array}{l}\text{= grammes in 1000 c.c. of} \\ \text{decinormal solution.}\end{array}\right.$$

The official (B.P.) sulphurous acid should contain 6·4 per cent. of hydrogen sulphite (H_2SO_3) corresponding to 5 per cent. of sulphurous anhydride (SO_2).

Arsenium.—About 0·1 gramme of *solid arsenious anhydride*, accurately weighed, should be dissolved in the usual quantity of water, heated to boiling, by aid of about 0·5 gramme of sodium bicarbonate. The arsenious anhydride is only partly, if at all, converted into arsenite; but the reaction with iodine occurs more readily in a solution which is not acid. When the liquid is quite cold, starch mucilage is added, and the iodine solution allowed to flow in until, after well stirring, a permanent blue colour is produced.—The official *arsenical solution* already containing some potassium carbonate must be neutralized by hydrochloric acid before the sodium bicarbonate is added. 10 cubic centimetres is a convenient quantity to operate with. To this should be added the usual quantity of water and about 0·6 gramme of sodium bicarbonate. After boiling and cooling, the titration is carried on as before.—About 10 cubic centimetres of the official *hydrochloric solution of arsenic* is also a convenient quantity to use. This quantity requires about 0·6 gramme of sodium bicarbonate. Water is added, and the titration performed as before. The following equation exhibits the reaction :—

$$\underbrace{As_4O_6}_{80)393{\cdot}28} + 10H_2O + \underbrace{4I_2}_{80)1007{\cdot}2} = 8HI + 4H_3AsO_4$$

$$\overline{\quad 4{\cdot}916 \quad} \qquad\qquad \overline{\quad 12{\cdot}59 \quad} \left\{ \begin{array}{l} = \text{grammes in 1000 c.c.} \\ \text{decinormal solution.} \end{array} \right.$$

Both the official solutions contain arsenium corresponding to 1 per cent. of arsenious anhydride.

In the foregoing operation, if ebullition be continued longer than is necessary for the solution of the arsenious anhydride, more sodium carbonate may be formed than will be reconverted into bicarbonate by the liberated carbonic acid; loss of iodine will then ensue. The results obtained by this method are therefore liable to vary slightly. E. J. Woolley showed that borax may be used with advantage in place of the sodium bicarbonate. The results of later experiments confirm this conclusion, and show that determinations can be carried out not only more accurately but more conveniently and quickly if borax is used, for it is a satisfactory solvent for arsenious anhydride and has not the disadvantage of being decomposed during the ebullition.

Sodium arsenate may be determined by treating it with sulphurous acid, boiling to expel the excess of the acid and then titrating with decinormal iodine solution as above.

$$Na_2HAsO_4 + H_2SO_3 = NaAsO_2 + NaHSO_4 + H_2O$$

Antimony is also raised in valency under the influence of nascent oxygen, iodine, or an equivalent acid radical. The following equation illustrates the reaction with tartar emetic and iodine. The student should make several determinations with, say, 20 c.c. of a solution containing 2 grammes of pure tartar emetic in 200 c.c. To the 20 c.c. add about an equal volume of concentrated solution of sodium bicarbonate and 2 c.c. of starch mucilage, and then the iodine solution, until, after stirring, the blue colour is fairly persistent. The whole operation should be conducted rapidly or a precipitate of antimonious hydroxide will be formed, and it is only when in solution that the antimony is properly attacked. This process is due to Mohr. It has been tested by Fresenius and in the Research Laboratory of the Pharmaceutical Society, and is trustworthy.

$$\underbrace{(KSbOC_4H_4O_6)_2,H_2O}_{40)659{\cdot}14} + \underbrace{2I_2}_{40)503{\cdot}6} + 3H_2O = 4HI + 2KHC_4H_4O_6 + 2HSbO_3$$

$$\overline{16{\cdot}478} \qquad \overline{12{\cdot}59} = \text{grammes in 1000 c.c. of decinormal solution.}$$

Sodium Thiosulphate.—About 0·4 gramme is a convenient quantity to employ. It is dissolved in water, starch mucilage added, and the iodine solution slowly run in, the whole being frequently stirred, until a permanent blue colour is produced.

In the previous reactions iodine has acted as an indirect oxidizing agent by uniting with the hydrogen and thus liberating the oxygen of water. In the present case it unites with an analogue of hydrogen, namely sodium, a new salt (sodium tetrathionate) being also produced, thus:—

$$\underbrace{2(Na_2S_2O_3,5H_2O)}_{20)492{\cdot}88} + \underbrace{I_2}_{20)251{\cdot}8} = 2NaI + Na_2S_4O_6 + 10H_2O$$

$$\overline{24{\cdot}644} \qquad \overline{12{\cdot}59} \left\{ = \begin{array}{l}\text{grammes in 1000 c.c. of}\\ \text{decinormal solution.}\end{array}\right.$$

The British Pharmacopœia requires absolute purity in the case of sodium thiosulphate.

Note.—Sodium thiosulphate may be obtained in a perfectly dry condition by treating the powdered salt with alcohol (90 or 95 per cent.), filtering, removing the excess of alcohol by washing with ether, and then expelling the ether by a current of dry air.

QUESTIONS AND EXERCISES

Give equations illustrative of the reactions on which the use of a standard volumetric solution of iodine is based.—From what point of view is iodine an oxidizing agent?—What reagent indicates the termination of the reaction between reducing substances and moist iodine?—How much sulphurous anhydride will cause the absorption of 2·518 parts of iodine in the volumetric reaction? *Ans.*, 0·6358.—What quantity of iodine will be required, under appropriate conditions, to oxidize 5 parts of arsenious anhydride? *Ans.*, 12·805.—Find by calculation the amount of sodium thiosulphate which will react with 13 parts of iodine in volumetric analysis. *Ans.*, 25·446.

VOLUMETRIC SOLUTION OF POTASSIUM BICHROMATE

(Potassium Bichromate, $K_2Cr_2O_7 = 292·3$.)

When used as an oxidizing agent in acid solution, potassium bichromate yields the whole of its oxygen to the hydrogen of the accompanying acid, a corresponding quantity of acid radical being set free—four-sevenths of this radical immediately combining with the potassium and chromium of the bichromate, three-sevenths becoming available for oxidation. Ferrous salts may thus be converted into ferric with sufficient rapidity and exactitude to admit of the determination of an unknown quantity of iron by a known quantity of the bichromate.

$$K_2Cr_2O_7 + 8H_2SO_4 + 6FeSO_4 = 2KHSO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Fe_2(SO_4)_3$$

The volumetric solution is made by dissolving 4·87 grammes ($\frac{1}{60}$ of the formula weight in grammes) of potassium bichromate in water, and diluting to one litre. It is used in determining the quantity of ferrous iron present in a preparation. It is known that the whole of the ferrous has been converted to ferric salt when a small drop of the liquid placed in contact with a drop of a fresh and very dilute solution of potassium ferricyanide, on a white plate, no longer produces a blue colour.

If the bichromate employed in making this solution is not known to be pure and dry, the concentration of the solution may be checked by dissolving an accurately weighed piece of pianoforte wire (0·4 or 0·5 gramme) in dilute sulphuric acid in a small flask, warming, and then adding the solution of bichromate until conversion is effected.

The reactions which take place may be thus represented :—

$$\underbrace{6Fe}_{\substack{60)333{\cdot}6 \\ \overline{\quad 5{\cdot}56}}} + 6H_2SO_4 = \underbrace{6FeSO_4}_{\substack{60)905{\cdot}64 \\ \overline{\quad 15{\cdot}094}}} + 6H_2$$

$$\underbrace{6FeSO_4}_{\substack{60)905{\cdot}64 \\ \overline{\quad 15{\cdot}094}}} + \underbrace{K_2Cr_2O_7}_{\substack{60)292{\cdot}3 \\ \overline{\quad 4{\cdot}871}}} + 8H_2SO_4 = 2KHSO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Fe_2(SO_4)_3$$

$4{\cdot}871$ = grammes in 1000 c.c. decinormal solution.

It is evident that 5·56 grammes of iron are equivalent in the reactions to 4·871 grammes of bichromate (*i.e.*, to 1000 c.c. of the standard solution). Now supposing that 0·5 gramme of pianoforte wire has been employed, and the quantity of solution of bichromate of unknown strength used has been 88 c.c. ; how many c.c. of this solution contain 4·871 grammes of bichromate, that is, how many c.c. will be required to oxidize ferrous salt containing 5·56 grammes of iron ? By calculation it is found that 978·5 c.c. contain 4·871 grammes of bichromate, and are equivalent to 1000 c.c. of standard solution. It might be employed without being diluted, or, better, be diluted to official standard (decinormal) strength.

For standardizing the solution of bichromate, instead of iron wire, the light-green crystals of the double *ammonium ferrous sulphate* ($(NH_4)_2SO_4,FeSO_4,6H_2O = 389{\cdot}44$) may be used, for it is a very stable salt.

Special care should be taken in all these determinations of substances readily oxidized to avoid atmospheric oxidation. Flasks may be loosely corked, or corked closely with a gas exit-tube passing just beneath the surface of a little mercury or sodium carbonate solution, and in all cases the titration should be performed quickly. When standardizing with iron wire, any slight oxidation may be remedied by addition of a fragment of zinc, the last portions of which must be removed or dissolved before the titration is commenced.

The ferrous salt in the following substances may be determined by this solution.

Ferrous sulphate.—Use 1 to 2 grammes. Dissolve the sulphate in water and add excess of sulphuric acid ; the preceding equation indicates the reaction.

Iron Arsenate.—Dissolve 1 to 2 grammes in excess of dilute sulphuric or hydrochloric acid. Sulphuric acid is preferable, because ferrous sulphate absorbs oxygen much less readily than ferrous chloride. The reaction that takes place is shown in the following equation, the ferrous arsenate being converted into ferric arsenate:—

$$\underbrace{2Fe_3(AsO_4)_2}_{\substack{60)885\cdot68 \\ \overline{14\cdot761}}} + 8H_2SO_4 + \underbrace{K_2Cr_2O_7}_{\substack{60)292\cdot3 \\ \overline{4\cdot871}}} \left\{ \substack{\text{= grammes in 1000 c.c.} \\ \text{decinormal solution.}} \right. =$$

$$2KHSO_4 + Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + 4FeAsO_4 + 7H_2O$$

Iron arsenate, B.P., is supposed to contain about 10 per cent. of anhydrous ferrous arsenate, or 12½ per cent. of the hydrous arsenate, $Fe_3(AsO_4)_2, 6H_2O$. The compound is more nearly a ferric than a ferrous arsenate.

Instead of determining the iron present in the ferrous state in iron arsenate, by means of volumetric solution of potassium bichromate, Nicholls (*P.J.* [4] **17**, 163) advocates determining the arsenium in it. His process consists in distilling 0·13 grm. of the sample twice or thrice with concentrated hydrochloric acid in presence of excess of ferrous sulphate and ferric chloride (so as to obtain the arsenium as arsenious chloride), exactly neutralising the distillate with caustic soda, and titrating the arsenite so formed with standard solution of iodine in presence of excess of sodium bicarbonate. The process is also applicable to sodium arsenate.

Iron Phosphate.—Operate upon 1 to 2 grammes. Proceed as with arsenate. The following equation indicates the reaction, the ferrous phosphate being converted into ferric phosphate:—

$$\underbrace{2Fe_3(PO_4)_2}_{\substack{60)710\cdot88 \\ \overline{11\cdot848}}} + 8H_2SO_4 + \underbrace{K_2Cr_2O_7}_{\substack{60)292\cdot3 \\ \overline{4\cdot871}}} \left\{ \substack{\text{= grammes in 1000 c.c.} \\ \text{of decinormal solution.}} \right. =$$

$$2KHSO_4 + Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + 4FePO_4 + 7H_2O$$

The official (B.P.) requirement is about one-third of its weight of anhydrous ferrous phosphate, or 47 per cent. of the hydrous $Fe_3(PO_4)_2, 8H_2O$.

Saccharated Iron Carbonate.—Proceed as with arsenate, using about the same quantity;—

$$\underbrace{6FeCO_3}_{\substack{60)690{\cdot}9\\ \overline{\quad 11{\cdot}515\quad}}} + 14H_2SO_4 + \underbrace{K_2Cr_2O_7}_{\substack{60)292{\cdot}3\\ \overline{\quad 4{\cdot}871\quad}}} \left\{ \substack{\text{=grammes in 1000 c.c. of}\\ \text{decinormal solution.}} \right. =$$

$$2KHSO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 13H_2O + 6CO_2$$

The official (B.P.) strength in ferrous carbonate is "about one-third." Commercial samples yield from 20 to 30, and sometimes 35 per cent., according to the care with which oxidation has been prevented. The theoretical percentage obtainable from the ingredients is 45·5, the quantity that would be present if the compounds were anhydrous and unoxidized—conditions never obtained in practice. The British Pharmacopœia directs that phosphoric acid be used to dissolve the saccharated ferrous carbonate; the reason for this is that dilute hydrochloric or sulphuric acid converts ordinary sugar into inverted sugar, which is easily attacked by chromic acid.

Magnetic Iron Oxide.—Use about the same quantity as of arsenate or phosphate, and proceed in the same manner. The reaction may thus be shown:—

$$\underbrace{6Fe_3O_4}_{\substack{60)1381{\cdot}92\\ \overline{\quad 23{\cdot}032\quad}}} + 32H_2SO_4 + \underbrace{K_2Cr_2O_7}_{\substack{60)292{\cdot}3\\ \overline{\quad 4{\cdot}871\quad}}} \left\{ \substack{\text{= grammes in 1000 c.c. of}\\ \text{standard solution.}} \right. =$$

$$2KHSO_4 + Cr_2(SO_4)_3 + 9Fe_2(SO_4)_3 + 31H_2O$$

Absolutely pure magnetic oxide of iron contains 31 per cent. of ferrous oxide. Oxidation occurs, however, during manufacture, as in the case of the ferrous salts just described.

Note.—The use in quantitative analysis of this volumetric solution of potassium bichromate admits of great extension. The student should at least employ it in the case of a few iron ores.

VOLUMETRIC SOLUTION OF POTASSIUM PERMANGANATE

(Potassium Permanganate, $KMnO_4 = 156{\cdot}87$.)

Dissolve 3·137 grammes ($\frac{1}{50}$ of the formula weight in grammes) of potassium permanganate in water and dilute to one litre. The solution is then standardized by means of a weighed quantity of pianoforte wire or of ammonium ferrou sulphate as described under potassium bichromate.

$$\underbrace{10\text{Fe}}_{\begin{array}{r}100)556\\ \hline 5{\cdot}56\end{array}} + 10\text{H}_2\text{SO}_4 = \underbrace{10\text{FeSO}_4}_{\begin{array}{r}100)1509{\cdot}4\\ \hline 15{\cdot}094\end{array}} + 10\text{H}_2$$

$$\underbrace{10\text{FeSO}_4}_{\begin{array}{r}100)1509{\cdot}4\\ \hline 15{\cdot}094\end{array}} + \underbrace{2\text{KMnO}_4}_{\begin{array}{r}100)313{\cdot}74\\ \hline 3{\cdot}1374\end{array}} + 9\text{H}_2\text{SO}_4 =$$

$3{\cdot}1374$ = grammes in 1000 c.c. standard solution.

$$2\text{KHSO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{Fe}_2(\text{SO}_4)_3$$

This solution may be used in nearly all cases for whic the volumetric solution of potassium bichromate has bee recommended. It must not be used in presence of hydro-chloric acid, as this acid is itself attacked by permanganat with production of water and chlorine.

Oxalic acid and other oxalates may be determined by mean of this standard solution of permanganate. About 0· gramme of crystallized oxalic acid or about 0·25 gramm of ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4,\text{H}_2\text{O}$, may be dissolved i water, a small quantity of dilute sulphuric acid added, th solution warmed to about 60° C., and the volumetric solutio of permanganate run in from a burette until a slight bu permanent pink coloration, due to excess of permanganate is produced.

$$\underbrace{5(\text{H}_2\text{C}_2\text{O}_4,2\text{H}_2\text{O})}_{\begin{array}{r}100)625{\cdot}50\\ \hline 6{\cdot}255\end{array}} + \underbrace{2\text{KMnO}_4}_{\begin{array}{r}100)313{\cdot}74\\ \hline 3{\cdot}174\end{array}} + 4\text{H}_2\text{SO}_4 =$$

$3{\cdot}174$ = grammes in 1000 c.c. standard sol

$$2\text{KHSO}_4 + 2\text{MnSO}_4 + 18\text{H}_2\text{O} + 10\text{CO}_2$$

It is obvious that if pure crystallized oxalic acid can b obtained this may be used as a means of standardizing th potassium permanganate solution. In the British Pharma copœia the purity of *Potassii permanganas* is determined b means of oxalic acid. "Each gramme dissolved in wate and acidulated with 5 cubic centimetres of diluted sulphur acid, should require for complete decolorization 31·2 cubi centimetres of an aqueous solution containing 62·55 gramm of pure crystallized oxalic acid per litre."

QUESTIONS AND EXERCISES

Write equations explanatory of the oxidizing action of potassium bichromate.—One hundred c.c. of an aqueous solution of potassium bichromate contain $\frac{1}{600}$ of the formula weight of the salt in grammes; with what weight of metallic iron, dissolved in hydrochloric acid, will this volume react? *Ans.*, 0·556 grammes.—If 3 grammes of impure crystallized ferrous sulphate dissolved in acidulated water, require 93 c.c. of the standard solution of bichromate for complete conversion into ferric salt, what percentage of ferrous sulphate is present? *Ans.*, 85·6.—How much potassium bichromate is required for the conversion of 10 parts of crystallized ferrous sulphate into ferric salt? *Ans.*, 1·763.—Show what quantity of pure ferrous carbonate is indicated by 1·475 part of bichromate as applied in volumetric analysis. *Ans.*, 3·48.—What quantity of official saccharated iron carbonate is equivalent to 0·7375 part of bichromate in the volumetric reaction? *Ans.*, 5·2.

DETERMINATION OF SUBSTANCES READILY REDUCED

Any substance which quickly yields a definite quantity of oxygen may be quantitatively tested by ascertaining how much of a reducing agent of known power must be added to a given quantity before complete reduction is effected. The chief compounds which may be used for this absorption of oxygen (deoxidizers or reducing agents, as they are commonly termed) are sodium thiosulphate, sulphurous acid, oxalic acid, arsenious acid. The first-named is officially used; it is only used in the estimation of free iodine, and, indirectly, of chlorine and chlorinated compounds. Iodine and chlorine are regarded as oxidizing agents, because their great affinity for hydrogen enables them to become powerful indirect oxidizers in presence of water.

Standard Solution of Sodium Thiosulphate

(Sodium Thiosulphate crystallized, $Na_2S_2O_3,5H_2O = 246·44$.)

Dissolve about 28 grammes of sodium thiosulphate in a litre or less of water. Fill a burette with this solution, and allow it to flow into a beaker containing, say, 15 c.c. of the volumetric solution of iodine until the brown colour of the iodine is just discharged—or, starch being added, until the blue starch iodide is decolorized. (The latter affords the more delicate indication.) When iodine and sodium thiosulphate react, two atoms of iodine remove two of sodium from two molecules of the sodium thiosulphate, sodium tetrathionate being formed, thus :—

$$\underbrace{I_2}_{20)\underline{251{\cdot}8}} \quad + \quad \underbrace{2(Na_2S_2O_3,5H_2O)}_{20)\underline{492{\cdot}88}} = 2NaI + Na_2S_4O_6 + 10H_2O$$

$12{\cdot}59$ {=grms. of iodine in 1000 c.c. $24{\cdot}644$ = grammes of thiosulphate in 1000 c.c.

Now suppose the number of c.c. required to completely react with the 15 c.c. of standard iodine were 14 c.c., how many c.c. of this thiosulphate solution would be equivalent to 1000 c.c. of the volumetric solution of iodine? In other words, how many c.c. contain 24·644 grammes of thiosulphate? 933 c.c. of the solution of sodium thiosulphate under examination contain 24·644 grammes of the salt, and are equivalent to 1000 c.c. of the official volumetric solution. The 933 c.c. can be diluted to 1000 c.c. or used without dilution. In either case its concentration would, as usual, be recorded on the label. The following substances may be determined by means of sodium thiosulphate solution of known concentration.

A solution of sodium thiosulphate containing 24·644 grammes of sodium thiosulphate per litre is sometimes spoken of as a decinormal solution, as each c.c. is equivalent to 1 c.c. of the decinormal solution of iodine.

Solution of Chlorine.—About 10 grammes may be taken. Excess of potassium iodide is added—that is, to 10 grammes of solution of chlorine, about half a gramme of iodide. A quantity of iodine is set free by the chlorine exactly in proportion to their atomic weights. The titration is then conducted as already described. The following equations show the reactions :—

$$\underbrace{Cl_2}_{\substack{20)\underline{70{\cdot}38}\\ 3{\cdot}519}} \quad + \quad 2KI \quad = \quad \underbrace{I_2}_{\substack{20)\underline{251{\cdot}8}\\ 12{\cdot}59}} \quad + \quad 2KCl$$

$$\underbrace{I_2}_{\substack{20)\underline{251{\cdot}8}\\ 12{\cdot}59}} + \underbrace{2(Na_2S_2O_3,5H_2O)}_{\substack{20)\underline{492{\cdot}88}\\ 24{\cdot}644}} = 2NaI + Na_2S_4O_6 + 10H_2O$$

$24{\cdot}644$ = grammes in 1000 c.c. decinormal solution.

It is evident, then, that 1000 c.c. of decinormal solution of sodium thiosulphate, or a corresponding quantity of a solution of different concentration, is equivalent to 3·519 grammes of chlorine.

Iodine.—Solid iodine is dissolved in solution of potassium iodide, and titrated as already described. About 0·2 gramme is a convenient quantity to employ. 1000 c.c. of decinormal thiosulphate solution is equivalent, as seen in the equation, to 12·59 of iodine. It is assumed in this operation that the iodine has been shown by qualitative analysis to be free from chlorine and bromine; for these elements resemble iodine in reacting with sodium thiosulphate, hence would reckon as iodine in a volumetric assay. The official iodine (*Iodum*, B.P.) should contain 100 per cent.

Chlorinated Lime.—Operate on from 0·1 to 0·2 gramme. Dissolve in water, and add excess of potassium iodide and dilute hydrochloric acid. 0·1 to 0·2 gramme of chlorinated lime requires 0·4 to 0·8 gramme of potassium iodide. The following equations show the reactions :—

$$CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2;$$
$$\text{or,} \quad CaOCl_2 + H_2SO_4 = CaSO_4 + H_2O + Cl_2$$

The chlorine thus set free liberates an equivalent amount of iodine, and this is titrated as before. (*See* the equations for the solution of chlorine, p. 742.) This chlorine, liberated from chlorinated lime by acids, is its available chlorine for indirect oxidizing action. It should correspond (B.P.) to at least 33 per cent.

Solution of Chlorinated Lime.—About 2 grammes is a convenient quantity to use. 1 gramme of potassium iodide and excess of acid should be added, and the available chlorine determined as in the case of the solid. The official (B.P.) requirement is 2 to 3 per cent. of available chlorine.

Solution of Chlorinated Soda.—About 2 grammes are mixed with the usual quantity of water, and 1 gramme of potassium iodide and excess of acid added. The available chlorine is determined as in the case of chlorinated lime. The reaction by which the chlorine is evolved is familiar :—

$$NaCl,NaOCl + 2HCl = 2NaCl + H_2O + Cl_2$$

The action of the liberated chlorine on the potassium iodide and the iodine on the thiosulphate solution has been described under "solution of chlorine." The official (B.P.) requirement is about 2½ per cent. of available chlorine.

Sodium thiosulphate may also be used for the determination of iron in ferric compounds. This method is based on the fact that when ferric chloride is digested with potassium iodide, it is reduced to ferrous chloride. Some of the potassium iodide is decomposed by the chlorine thus released, and an equivalent quantity of iodine is liberated. The ferric salt should be dissolved in hydrochloric acid, the solution nearly neutralized with caustic potash or soda solution, transferred to a well-stoppered flask, and excess of a concentrated solution of potassium iodide added. The flask should then be closely stoppered and heated to 50° or 60° C. on a water-bath for about 20 minutes; iodine is liberated, and dissolves in the excess of potassium iodide. After cooling the solution and adding mucilage of starch, the thiosulphate solution is run in until the blue colour disappears. The following equations show the reactions:—

$$\underbrace{2FeCl_3}_{\begin{array}{r}20)322{\cdot}34\\ \hline 16{\cdot}117\end{array}} + 2KI = 2FeCl_2 + 2KCl + I_2$$

$$I_2 + \underbrace{2(Na_2S_2O_3,5H_2O)}_{\begin{array}{r}20)494{\cdot}88\\ \hline 24{\cdot}644 \text{ = grammes in 1000 c.c. of decinormal solution.}\end{array}} = 2NaI + Na_2S_4O_6 + 10H_2O$$

Thus it is evident that 1000 c.c. of decinormal solution of sodium thiosulphate are equivalent to 16·117 grammes of ferric chloride. The following official compounds may be examined by this method:—Ferri et Ammonii Citras, Ferri et Quininæ Citras, Ferri Phosphas, Ferrum Redactum, Ferrum Tartaratum, Liquor Ferri Acetatis, Liquor Ferri Perchloridi, Liquor Ferri Pernitratis, Liquor Ferri Persulphatis, and Tinctura Ferri Perchloridi.

QUESTIONS AND EXERCISES

For what purpose is the volumetric solution of sodium thiosulphate used?—On what reaction is based the quantitative employment of sodium thiosulphate?—How much sodium thiosulphate is required to show the presence of 10 parts of iodine? *Ans.*, 19·574.—Calculate the quantity of chlorine 4·96 parts of sodium thiosulphate are equivalent to in volumetric analysis. *Ans.*, 0·708.—Describe the operations involved in the determination of the strength of bleaching-powders. —What indicator is used to show the termination of the reaction between iodine and sodium thiosulphate?

QUESTIONS, WITH ANSWERS FOR VERIFICATION

Calculate how much potassium bicarbonate is contained in an eight-ounce bottle of medicine, seven fluid drachms of which are neutralized by 2·72 grains of pure sulphuric acid. *Ans.*, 36·3 grains. —A sample of soda-ash is said to contain 78 per cent. of pure anhydrous sodium carbonate: if the statement be true, how much of the official volumetric solution of sulphuric acid will neutralize 5 grammes of the specimen? *Ans.*, 74 c.c.—2·69 grammes of commercial sulphuric acid are neutralized by 43·5 c.c. of the official volumetric solution of soda; how much acid of 96·8 per cent. is present? *Ans.*, The 2·69 contain 2·05.—Four c.c. of a litre and a half of concentrated hydrocyanic acid are equivalent to 89 c.c. of the official volumetric solution of silver nitrate; to what volume must the bulk of the acid be diluted for the production of acid of pharmacopœial strength? *Ans.*, 8·894 litres.—3·18 grammes of a powder containing arsenious anhydride require for complete reaction 84 c.c. of a volumetric solution of iodine, which is 1·43 per cent. weaker than the standard solution of the British Pharmacopœia; what percentage of pure arsenious anhydride is contained in the powder? *Ans.*, 12·716.—How much pure metal is present in a sample of iron 1 gramme of which, dissolved in dilute sulphuric acid, is exactly attacked by 95·7 c.c. of a volumetric solution of potassium bichromate which is 0·6 per cent. stronger than the official solution?

GRAVIMETRIC ANALYSIS

(*For preliminary remarks on the general principles of gravimetric analysis and the relation of gravimetric and volumetric analyses to each other, see pages* 710 *and* 711.)

DETERMINATION OF METALLIC RADICALS

POTASSIUM

Outline of the process.—This element is usually determined in the form of potassium chloroplatinate. Qualitative analysis having proved the presence of potassium and other radicals in a substance, a small quantity of the material is accurately weighed, dissolved, and the other metallic radicals removed by appropriate means: the precipitates are well washed, in order that no trace of the potassium salt be lost, the resulting liquid concentrated over a water-bath (to avoid loss that would occur mechanically during ebullition), hydrochloric acid added if necessary, solution of chloroplatinic acid poured in, and evaporation continued to dryness: excess of the precipitant is then dissolved out by adding, to the dried residue, alcohol (90 per cent.) mixed with half its bulk of ether (a mixture in which the chloroplatinate is insoluble), the whole carefully poured on to a tared and dried filter, washed with the mixture of alcohol and ether till every trace of chloroplatinic acid is removed, and dried and weighed; from the weight of potassium chloroplatinate the proportion of potassium, or equivalent quantity of a salt of potassium, is ascertained by calculation.

> *Note.*—From this short description it will be seen, first, that the chemistry of quantitative analysis is the same as that of qualitative; and secondly, that the principle of gravimetric is the same as that of volumetric quantitative analysis:—the combining proportions of substances being known, unknown quantities of elements may be ascertained by calculation from known quantities of their compounds.

Apparatus.—In addition to a very delicate balance, accurate weights and the common utensils, a few special instruments are used in quantitative manipulation; some of these may be prepared before proceeding with the determination of potassium.

Filter-paper may be of the kind known as "Swedish," the texture of which is of the requisite degree of closeness, and its ash small in amount. A large number of circular pieces of one size, six to eight centimetres in diameter, should be cut ready for use. In delicate experiments, where a precipitate on a filter has to be ignited and the paper subsequently burnt, the weight of the ash of the filter must be deducted from the weight of the residue. The ash is determined by burning ten or twenty of the cut filters. These are folded into small compass, a piece of platinum wire twisted a few times round the packet so as to form a cage, the whole held by the free end of the wire over a weighed porcelain crucible placed on the centre of a sheet of glazed paper, and the bundle ignited by a spirit-lamp or Bunsen flame. The flame is allowed to impinge against the charred mass till it falls into the crucible below, any stray fragments on the sheet being carefully brushed into the crucible, the latter placed over a flame till carbon has all been burnt off, and nothing but ash remains; the whole cooled, weighed, and the weight of the crucible deducted. The weight of the residue divided by the number of pieces used gives the average weight of ash in each filter.

The necessity for carrying out the operations described in the preceding paragraph has been almost entirely obviated by the introduction of the so-called ashless filters—circular filter papers of various sizes, from which the mineral matter which gives rise to the ash has been removed, practically completely, by extraction with hydrochloric and hydrofluoric acids.

For the complete retention of certain exceeding finely divided precipitates, such as barium sulphate, calcium oxalate, cuprous thiocyanate, etc., filter papers possessing the closest texture must be employed.

A pair of weighing tubes (fig. 50), for holding dried filters, may be made from two test-tubes, one fitting closely within the other. About five centimetres of the closed end of the outer and seven of the inner are cut off by leading a crack round the tube with a pencil of incandescent charcoal, and the sharp edges fused in the blow-pipe flame. A filter, after drying, is quickly folded and placed in the narrower tube, the mouth of which is then closed by the wider tube. This prevents reabsorption of moisture from the air. *A pair of watch-glasses*, having accurately ground edges and clamped as shown in figure 51, forms a convenient arrangement for weighing filters, etc. *Small weighing bottles*, light stoppered bottles having wide mouths, are also useful.

FIG. 50. A Pair of Weighing-tubes.

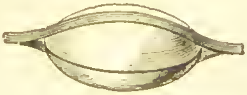

FIG. 51. Clamped Watch-glasses for Weighing.

The wash-bottle (fig. 52), holding the *alcohol and ether,* is a common flask, through the cork of which a short straight tube passes. The outer end of the tube should be sufficiently narrowed to enable it to deliver a very fine stream of the liquid. The flask being inverted, the warmth of the hand expands the air and vapour to a sufficient extent to force out the liquid.

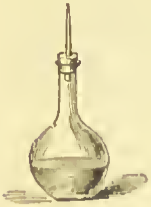
FIG. 52.

The ordinary wash-bottle for quantitative operations should be formed of a flask in which water may be boiled, fitted up as usual (*see* p. 121).

A water-oven is the best form of drying-apparatus. It is a small square copper vessel, jacketed on five sides and having a door on the sixth; water is poured into the space between the inner and outer casing, and the whole placed over a gas-lamp or other source of heat, moist air and steam escaping by appropriate apertures. Holes in the top an inch or two in diameter, covered when not in use, serve for the reception of small dishes containing liquids to be evaporated. Drying at higher temperatures than the boiling-point of water may be practised by using oil or paraffin instead of water, inserting a thermometer in the oil; or by the use of an *air-bath,* which is simply a metal box provided with a door and heated by means of a Bunsen flame.

A desiccator is a glass vessel in which a substance to be dried, or to be cooled in a dry atmosphere, is enclosed along with a powerful dehydrating agent such as concentrated sulphuric acid, potassium hydroxide, or fused calcium chloride (figs. 53 and 54).

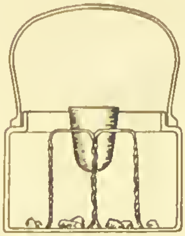
FIG. 53.—Desiccator.

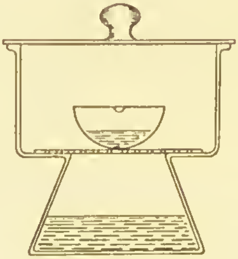
FIG. 54.—Desiccator.

Pure distilled water must be used in all quantitative determinations.

Note.—In practising the operations of quantitative analysis, experiments should at first be conducted on definite salts of known composition, for the accuracy of results may then be tested by calculation.

Determination of potassium in the form of potassium chloroplatinate.—Select two or three crystals of pure potassium nitrate, powder them in a clean mortar, dry the powder by gently heating in a porcelain crucible over a flame for a few seconds, place about a couple of decigrammes (0·2 grm.) of the powder in a counterpoised watch-glass, accurately weigh the selected quantity, transfer to a small dish, letting water from a wash-bottle flow over the watch-glass and run into the dish, warm the dish till the nitrate is dissolved, acidulate with hydrochloric acid, add excess of aqueous solution of chloroplatinic acid (a quantity of solution containing about 0·5 grm. of H_2PtCl_6), evaporate to dryness on a water-bath. While evaporation is going on, place a filter and the weighing-tubes in the water-oven, exposing them to a temperature of 100° C. for about half an hour; fold the filter and insert it in the tubes, place them in a desiccator to cool, and when cold accurately note their weight. Arrange the weighed filter in a funnel over a beaker. Transfer the dried and cooled chloroplatinate from the dish to the filter by moistening the residue with the mixture of alcohol and ether and, when the salt is loosened, pouring the contents of the dish into the paper cone. Any salt still adhering may be freed by the finger, which, together with the dish, should be washed in the stream of alcohol and ether, the rinsings at once flowing into the filter. The filtrate should have a yellowish-brown colour, due to the excess of chloroplatinic acid. If it is colourless, an insufficient amount of the precipitant has been added, and the whole operation must be repeated. After washing with the mixture of alcohol and ether until the liquid is no longer coloured by chloroplatinic acid, the precipitate and filter are dried in the water-oven, folded and placed in the weighing-tubes, the tubes placed open in the drying-oven for a short time, removed, closed, allowed to cool and then weighed. The drying and weighing when cold should be repeated until the whole ceases to alter, the final weight being noted.

Analytical memoranda may have the following form :—

Watch-glass and substance . . .
Watch-glass . . . .
Substance .

Weighing-tubes, filter, and salt . .
Weighing-tubes and filter . . .
K_2PtCl_6 .

The calculations are simple :—

$$\text{As}\left\{\begin{matrix}K_2PtCl_6\\=482{\cdot}1\end{matrix}\right\}\text{is equivalent to}\left\{\begin{matrix}2KNO_3\\=200{\cdot}82\end{matrix}\right\},$$

$$\text{so}\left\{\begin{matrix}\text{the weight of}\\\text{chloroplatinate}\\\text{obtained}\end{matrix}\right\}\text{is equivalent to } x.$$

x will be the weight of pure potassium nitrate in the quantity of substance operated on. x should in the present instance be identical with the weight of substance taken, because, for educational purposes, the pure nitrate is under examination. Only after analyses of pure substances have yielded the operator results practically identical with those obtained by calculation, can analyses of substances of unknown degree of purity be undertaken with confidence. A table of atomic weights, from which to find molecular weights, is given in the Appendix.

Platinum Residues should be preserved, and the metal recovered from time to time (*see* p. 224).

Hot alcohol sometimes reduces chloroplatinic acid, the metal being thrown out of solution in a finely divided form, known as *platinum black;* only aqueous solutions, therefore, of this reagent should be used where heat is employed. Hence, also, in washing out excess of chloroplatinic acid with the mixture of alcohol and ether the application of heat should be avoided.

Proportional Weights of Equivalent Quantities of Potassium and some of its compounds.

Metal	K_2	77·66
Oxide	K_2O	93·54
Hydroxide (Caustic Potash)	2KOH	111·42

Carbonate (anhydrous)	K_2CO_3	137·21
Carbonate (crystalline)	K_2CO_3 + 16 % Aq.	163·36
Bicarbonate	$2KHCO_3$	198·76
Nitrate	$2KNO_3$	200·82
Chloroplatinate	K_2PtCl_6	482·1

SODIUM

Sodium is usually determined as sulphate. Accurately weigh a porcelain crucible and lid, place within it about 0·3 of pure powdered rock-salt, and again weigh, making a memorandum of the weights in a note-book. Add rather more concentrated sulphuric acid than may be considered sufficient to convert the chloride into acid sodium sulphate. Heat the crucible gradually, the flame being first directed against the side of the crucible to avoid violent ebullition, until fumes of acid are no longer evolved, towards the end of the operation dropping in one or two fragments of ammonium carbonate to facilitate complete expulsion of all excess of acid. When cold, weigh the crucible and contents. The weight of the crucible having been deducted, the amount of sulphate obtained should be the exact equivalent of the quantity of sodium chloride taken.

$$\underbrace{2NaCl}_{116\cdot14} + H_2SO_4 = \underbrace{Na_2SO_4}_{141\cdot1} + 2HCl$$

Proportional Weights of Equivalent Quantities of Sodium and some Sodium compounds.

Metal	Na_2	45·76
Oxide	Na_2O	61·64
Hydroxide (Caustic Soda)	$2NaOH$	79·52
Carbonate (anhydrous)	Na_2CO_3	105·31
Carbonate (crystals)	$Na_2CO_3,10H_2O$	284·11
Bicarbonate	$2NaHCO_3$	166·86
Chloride	$2NaCl$	116·14
Sulphate (anhydrous)	Na_2SO_4	141·1
Sulphate (crystals)	$Na_2SO_4,10H_2O$	319·9

AMMONIUM

Salts of ammonium are, for purposes of quantitative analysis, generally converted into the chloroplatinate

$(NH_4)_2PtCl_6$, the details of manipulation being the same as those observed in the case of potassium (p. 749). About 0·15 gramme of pure, white, dry, ammonium chloride may be taken for experiment.

Composition of the Chloroplatinate.

		In formula wt.	In 100 parts.
Pt	193·3	193·30	43·900
Cl_6	35·19 × 6	211·14	47·951
N_2	13·94 × 2	27·88	6·332
H_8	1·0 × 8	8·00	1·817
		440·32	100·000

The proportion of nitrogen, or ammonium, in the chloroplatinate may also be ascertained from the weight of platinum left on ignition; indeed, this operation *must* be performed if methyl-ammonium or any other substituted ammonium be present. The heat must be applied slowly, or platinum will be mechanically carried off with the gaseous products of decomposition.

Proportional Weights of Equivalent Quantities.

Ammonia	$2NH_3$	33·88
Ammonium	$(NH_4)_2$	35·88
Ammonium chloride	$2NH_4Cl$	106·26
Chloroplatinate	$(NH_4)_2PtCl_6$	440·32
"Ammonium carbonate"	$(N_3H_{11}C_2O_5) \div 3 \times 2$	104·026
Ammonium sulphate	$(NH_4)_2SO_4$	131·22

BARIUM

Barium is determined in the form of anhydrous barium sulphate ($BaSO_4$). Ba = 136·4.

Process.—Dissolve 0·3 or 0·4 of pure crystallized and dried barium chloride or nitrate in about 100-150 c.c. of water in a beaker, heating to incipient ebullition, and slightly acidulating with hydrochloric or nitric acid. Heat some dilute sulphuric acid (prepared some days previously, so that any lead sulphate may have deposited) and add the hot acid to the barium solution in successive small quantities so long as a precipitate forms, keep the mixture hot for some time, set aside for half an hour, pass the supernatant liquid through a filter, gently boil the residue twice or thrice with acidulated water; finally collect the precipitate on the filter, removing adherent particles from the beaker by the finger, and cleansing by a stream of hot water from the wash-bottle. The precipitate must be washed with hot water until the filtrate no longer turns litmus-paper red or gives any cloudiness when tested with barium chloride. The filter with the barium sulphate, having been thoroughly drained, is dried in a warm place, usually by supporting the funnel in an inverted bottomless beaker over a sand-bath or hot plate.

The barium sulphate is now removed from the filter, heated to drive off every trace of moisture, and weighed. This is accomplished by placing a weighed porcelain crucible on a sheet of glazed paper, holding the filter over it, and carefully transferring the precipitate. The sides of the filter are then gently rubbed together and the detached powder dropped into the crucible, the paper folded, encased in two or three coils of one end of a platinum wire, and burnt over the crucible, the ash and any particles on the sheet of paper dropped into the barium sulphate, the open crucible exposed over a flame till its contents are quite white, covered, cooled, and weighed.

Note.—If the filter has not been freed by thorough washing from all traces of acid the paper will be brittle when dry, falling to pieces on being folded.

	Formulæ.	Formula Weights.
Barium chloride . . .	$BaCl_2,2H_2O$ . .	242·54
Barium nitrate . . .	$Ba(NO_3)_2$ . .	259·56
Barium sulphate . . .	$BaSO_4$ . . .	231·74

Composition of Barium Sulphate.

		In formula weight.	In 100 parts.
Ba . .	136·40 . .	136·40 .	. 58·86
S . .	31·82 . .	31·82 .	. 13·73
O_4 . .	15·88 × 4 . .	63·52 .	. 27·41
		231·74	100·00

In the first four or five educational experiments it is not essential to take filter-ash into account. Mistakes of manipulation due to inexperience may cause far greater errors.

CALCIUM

Calcium is usually precipitated as oxalate, the precipitate ignited, and the resulting carbonate weighed.

Process.—Dissolve 0·3 or 0·4 of dried colourless crystals of calc-spar in about a third of a litre of water acidulated with hydrochloric acid, heat the solution to near the boiling-point, add excess of boiling solution of ammonium oxalate, then ammonia until, after stirring, the liquid smells strongly of ammonia; set aside in a warm place for twelve hours. Carefully pour off the supernatant liquid, passing it through a filter; add hot water to the precipitate, set aside for half an hour, again decant, and, after once more washing, transfer the precipitate to the filter, allowing all contained fluid to pass through before a fresh portion is added. Wash the precipitate with hot water, avoiding a rapid stream, or the precipitate may be driven through the pores of the paper. Dry, transfer to a weighed crucible, and incinerate, as described for barium sulphate, and slowly heat the precipitate till the bottom of the crucible is just visibly red when seen in the dark. As soon as the residue is white or only faintly grey, remove the flame, cool, and weigh.

The resulting calcium carbonate should have the same weight as the calc-spar from which it was obtained. If loss has occurred, carbonic anhydride has probably escaped. In that case moisten the residue with water, and after a few minutes test the liquid with red litmus or turmeric paper; if an alkaline reaction is noticed, it is due to the presence of caustic lime. Add a small lump of ammonium carbonate, evaporate to dryness on a water-bath, and again ignite, this time being careful not to go beyond the prescribed temperature. The treatment may, if necessary, be repeated.

Proportional Weights of Equivalent Quantities of Calcium and some of its compounds.

Metal	Ca	39·71
Oxide (quicklime)	CaO	55·59
Hydroxide (slaked lime)	$Ca(OH)_2$	73·47
Carbonate	$CaCO_3$	99·26
Sulphate (anhydrous)	$CaSO_4$	135·05
Sulphate (crystalline or precipitated)	$CaSO_4,2H_2O$	170·81
Chloride	$CaCl_2$	110·09
Phosphate (of bones)	$Ca_3(PO_4)_2 \div 3$	102·59

MAGNESIUM

Process 1.—*The light or heavy magnesium carbonate* of pharmacy may be estimated by heating a weighed quantity to redness in a porcelain crucible. If it has the composition indicated by the formula given in the British Pharmacopœia, $3MgCO_3, Mg(OH)_2, 4H_2O$, it will yield 42 per cent. of magnesia (MgO). The official solution of magnesium carbonate in carbonic acid water (*Liquor Magnesii Carbonatis,* B.P.) should yield about 9 grammes of pure magnesium oxide per litre or about 4 grains per fluid ounce.

Process 2.—*The general form in which magnesium is precipitated* is as ammonium magnesium phosphate ($NH_4MgPO_4,6H_2O$); this, by heat, is converted into magnesium pyrophosphate ($Mg_2P_2O_7$). Accurately weigh a small quantity (0·4 to 0·5 gramme) of pure dry magnesium sulphate, dissolve it in two to three hundred cubic centimetres of cold water in a beaker, add ammonium chloride, ammonia, and sodium or ammonium phosphate, agitate with a glass rod (without touching the sides of the vessel, or crystals will firmly adhere to the rubbed portions), and set aside for twelve hours. Collect the precipitate on a filter, wash with water containing a tenth of its volume of the strongest solution of ammonia, until the filtrate no longer gives a precipitate with a solution of silver nitrate acidulated with nitric acid. Dry, transfer to a porcelain crucible, burn the filter in the usual way, heat slowly to redness, cool, and weigh.

Proportional Weights of Equivalent Quantities of some Magnesium compounds.

Pyrophosphate .	$Mg_2P_2O_7$	221·12
Sulphate . .	$2(MgSO_4,7H_2O)$ . . .	489·36
Oxide . . .	$2(MgO)$	80·12
Official carbonate .	$3MgCO_3,Mg(OH)_2,4H_2O \div 2$.	190·325

ZINC

Zinc is usually determined as oxide (ZnO), occasionally as sulphide (ZnS).

Process.—Dissolve a weighed quantity (0·5 to 0·6 gramme) of zinc sulphate in about half a litre of water in a beaker, heat to near the boiling-point, add solution of sodium carbonate in slight excess, boil, set aside for a short time; pass the supernatant liquid through a filter, gently boil the precipitate with more water, again decant; repeat these operations two or three times; collect the precipitate on the filter, wash, dry, transfer to a crucible, incinerate, ignite, cool, and weigh. 285·41 (= the formula weight) of sulphate should yield 80·79 (= the formula weight) of oxide.

MANGANESE

To ascertain its value for evolving chlorine from hydrochloric acid, a weighed quantity of finely powdered black

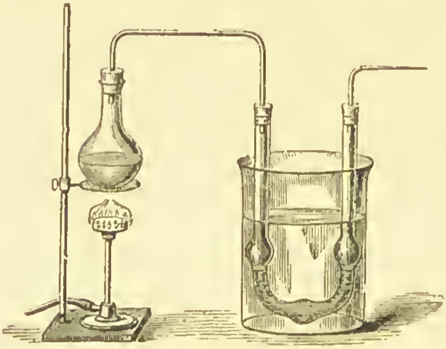

FIG. 55.

manganese oxide is heated in a small flask with pure hydrochloric acid (contained in an inner tube as for "oxalates" and "carbonates," p. 776), and the resulting chlorine conveyed into a U tube containing solution of potassium iodide. (*See* fig. 55.) The amount of iodine thus liberated is determined by means of the volumetric solution of sodium thiosulphate. 125·9 parts of iodine indicate 35·19 of chlorine.

Black manganese oxide may also be estimated by the reaction and apparatus described under "Oxalates," p. 778.

ALUMINIUM

Aluminium is always precipitated as hydroxide, $Al(OH)_3$, and weighed as oxide (Al_2O_3).

Process.—Dissolve about 2 grammes of pure dry ammonium-alum in half a litre of water, heat the solution, add ammonium chloride and a slight excess of ammonia, boil gently till the odour of ammonia has nearly disappeared, set aside for the hydroxide to deposit, pass the supernatant liquid through a filter, wash the precipitate three or four times by decantation, transfer to the filter, finish the washing, dry, burn the filter, ignite in a covered crucible, cool, and weigh.

$K_2SO_4, Al_2(SO_4)_3, 24H_2O$	941·94
$(NH_4)_2SO_4, Al_2(SO_4)_3, 24H_2O$	900·16
Al_2O_3	101·44
Per cent. of Al_2O_3 yielded by ammonium-alum . .	11·27

QUESTIONS AND EXERCISES

Give details of the manipulations observed in gravimetrically determining potassium or ammonium.—What quantity of sodium chloride is contained in a sample of rock-salt 0·351 gramme of which yields 0·426 of sodium sulphate? *Ans.*, 99·83 per cent.—To what weight of ammonium-alum is 0·888 gramme of ammonium chloroplatinate equivalent? *Ans.*, 1·817 gramme.—Find the weight of barium sulphate obtainable from 0·522 of barium nitrate? *Ans.*, 0·466.—Describe the usual method by which calcium is determined.—By what quantitative process may the official magnesium salts be analysed?—Calculate the proportion of pure zinc sulphate in a sample of crystals 0·574 gramme of which yield 0·161 gramme of oxide. *Ans.*, 99·4 per cent.—Ascertain the weight of alumina (Al_2O_3) which should be obtained from 1·812 gramme of ammonium-alum.

IRON

Iron and its salts are gravimetrically determined in the form of ferric oxide (Fe_2O_3).

Compounds containing organic acid radicals are simply incinerated, and the resulting oxide weighed. Thus 1 gramme of the official iron and ammonium citrate (*Ferri et Ammonii Citras*, B.P.) incinerated, with exposure to air, leaves 0·31 or 0·32 of ferric oxide. A small quantity of the salt is weighed in a tared covered porcelain crucible and the flame cautiously applied until vapours are no longer evolved. The lid is then removed, the crucible slightly inclined and exposed to a red heat until all carbonaceous matter has disappeared. After cooling, the residual ferric oxide is weighed. The potassium and iron tartrate (*Ferrum Tartaratum*, B.P.) is treated in the same manner, except that the ash must be washed in order to remove potassium carbonate produced during incineration, and again heated before weighing; 5 grammes should yield about 1·5 grammes of ferric oxide.

From other compounds of iron, soluble in water or acid, the iron is precipitated in the form of hydroxide, $Fe(OH)_3$ by solution of ammonia, and converted into oxide (Fe_2O_3), by ignition. Dissolve a piece (0·2 gramme) of the purest iron obtainable (piano-wire), accurately weighed, in dilute hydrochloric acid; add a few drops of nitric acid, and gently boil; add excess of ammonia, stir, set aside till the ferric hydroxide has deposited, pass the supernatant liquid through a filter, treat the precipitate three or four times with boiling water; transfer to the filter, wash till the filtrate yields no trace of chloride (for ammonium chloride will decompose ignited ferric oxide, with volatilization of ferric chloride), dry, ignite, and weigh. Iron in the official solutions (*Liquor Ferri Acetatis*, *Liquor Ferri Perchloridi Fortis*, *Liquor Ferri Pernitratis*, and *Liquor Ferri Persulphatis*) may be determined by this general gravimetric process.

The proportion of metallic iron in a mixture of iron and iron oxides may be determined by digestion in a concentrated solution of iodine and potassium iodide, which attacks the metal only. The reduced iron of pharmacy (*Ferrum Redactum*, B.P.) is in good condition so long as it contains 75 per cent. of free metal. Or (B.P.), "if 0·25 gramme be added to a hot solution of 1 gramme of copper sulphate in 15 cubic centimetres of water, in a flask that can immediately be well corked, and the whole be shaken occasionally during ten minutes, the liquid, after being rapidly filtered with the minimum of exposure to air, and acidulated with sulphuric acid, should not cease to yield a blue precipitate with solution of potassium ferricyanide until at least 33·7 cubic centimetres of the volumetric solution of potassium bichromate have been added." (*See* p. 231.)

Proportional Weights of Equivalent Quantities of Iron and some of its compounds.

Metal	Fe_2	111·2
Ferric oxide	Fe_2O_3	158·84
Ferric hydroxide	$2Fe(OH)_3$	212·48
Ferric chloride	$2FeCl_3$	322·34
Ferric sulphate	$Fe_2(SO_4)_3$	397·22
Ferrous sulphate	$2(FeSO_4,7H_2O)$	552·2

ARSENIUM

Arsenious anhydride (As_4O_6) and arsenious compounds are usually determined volumetrically (*see* p. 733), and sometimes arsenates also (*see* pp. 734 and 738), but the latter can also be precipitated as lead salt; "a solution of 1 gramme of sodium arsenate with 1 of glacial acetic acid, in 50 cubic centimetres of water, should require 2·03 grammes of lead acetate for complete precipitation." Arsenium can be wholly converted into hydrogen arsenide and determined quantitatively by absorbing the hydrogen arsenide in silver nitrate solution (p. 227). Towards the end of the operation, a solution of stannous chloride in hydrochloric acid is added to the contents of the vessel in which the gas is being evolved. This causes the precipitation of any arsenium still remaining in the solution, in a very finely divided state, in which it is readily attacked by the nascent hydrogen and converted into hydrogen arsenide (Schmidt).

Process 1.—With certain precautions arsenium may be precipitated and weighed as sulphide (As_2S_3). The pure, white arsenic in lump (about 0·2) is dissolved in a flask in a small quantity of water containing sodium or potassium bicarbonate, the liquid being heated. A slight excess of hydrochloric acid is then added, and hydrogen sulphide gas passed through the solution so long as a precipitate falls, the mouth of the flask being stopped by a plug of cotton-wool (to prevent undue access of air and consequent decomposition of the gas, resulting in precipitation of sulphur). The mixture is warmed in the flask and carbonic anhydride passed through it until the odour of hydrogen sulphide has nearly disappeared; the precipitate is collected on a tared filter, washed as quickly as possible with hot water containing a little hydrogen sulphide, dried in a water-oven, and weighed. 196·64 parts of white arsenic should yield 244·46 of arsenious sulphide.

Process 2.—*The arsenium must be present in the arsenic condition.* If the operator is not certain that this is the case, the solution must be warmed with a little hydrochloric acid and a few crystals of potassium chlorate added until a distinct chlorous odour is evolved—which is then allowed to escape by continued application of heat. To the solution thus obtained ammonia, which must produce no turbidity, is added in excess, and then magnesia mixture (*see* under "phosphates," p. 778). The solution is set aside for twenty-four or forty-eight hours. The precipitate is collected on a filter and washed with as little ammonia water (1 to 3) as possible until the filtrate no longer gives a reaction for chlorides. The precipitate is then dried on the filter, the filter-paper burned apart from the precipitate, and the whole gently ignited in a porcelain crucible, and weighed. This residue is magnesium pyro-arsenate, and has the formula $Mg_2As_2O_7$.

Note.—For the determination of minute quantities of arsenium in such liquids as beer, and in brewing materials and fuel, Thorpe's adaptation* of Bloxam's electrolytic method may be employed.

ANTIMONY

The metal is precipitated in the form of sulphide (Sb_2S_3), with the precautions observed in determining arsenium—a small quantity of tartaric acid, as well as hydrochloric, being added to prevent the precipitation of an oxysalt. If the hydrogen sulphide be passed through a *hot* solution, the particles of precipitate aggregate better and may be more quickly filtered and washed. The experiment may be performed with about half a gramme of pure tartar-emetic; the salt should yield nearly half its weight of sulphide. According to Fresenius, the sulphide dried at 100° C. still contains 2 per cent. of water, and must be heated in a current of carbonic anhydride, until it turns from an orange to a black colour, before all moisture is expelled. The purity of tartar-emetic (*Antimonium Tartaratum*) may be determined by the above process. Of the *Antimonium Sulphuratum*, B.P., it is stated that "3 grammes moistened and warmed with successive portions of nitric acid until red fumes cease to be evolved, and then dried and heated to redness, should leave a white residue weighing about 2 grammes." This white residue consists of the oxide, Sb_2O_4.

For the volumetric determination of antimony in antimonious salts, *see* p. 735.

COPPER

Copper may be determined as metal or as cupric oxide (CuO). Sometimes it is precipitated and weighed as cuprous thiocyanate or precipitated as cupric sulphide and weighed as cuprous sulphide.

Process 1.—Dissolve about half a gramme of dry crystallized cupric sulphate in a small quantity of water, in a tared porcelain crucible or beaker, acidulate with hydrochloric acid, introduce a fragment or two of pure zinc, cover the vessel with a watch-glass, and set aside till evolution of hydrogen has ceased and the still acid liquid is colourless. The copper is then washed with hot water by decantation until no trace of acid remains, the precipitate is drained, rinsed with alcohol, dried in the water-oven, cooled, and weighed.

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* Communicated to the Chemical Society of London on June 17, 1903. *Journ. Chem. Soc.*, 83, 969 and 974.

Process 2.—From a solution acidulated with sulphuric acid and placed in a platinum crucible, copper may be entirely deposited in a coherent form by a weak current of electricity, the crucible being connected with the zinc pole of the battery, a platinum spatula suspended in the solution forming the positive pole. The crucible may afterwards be freed from the deposited copper by means of nitric acid.

Process 3.—About 0·75 gramme of cupric sulphate is dissolved in half a litre of water, and the liquid boiled; dilute solution of caustic potash or caustic soda is then added till no more precipitate falls, ebullition continued for a short time, and the beaker set aside; the supernatant liquid is decanted, the precipitate boiled with water twice or thrice, collected on a filter, washed, dried, transferred to a porcelain crucible, the filter incinerated, added to the precipitate in the crucible and moistened with a drop of nitric acid; the whole is finally heated strongly, cooled, and weighed. This process can only be employed in absence of organic substances, as certain organic compounds such as tartaric and citric acids prevent the complete precipitation of the cupric oxide.

247·86 parts of crystallized cupric sulphate should yield 79·0 of oxide, or 63·12 of metal.

The cupric oxide obtained as above almost always weighs more than the theoretical proportion as it is practically impossible to wash it free from alkali.

Process 4.—About half a gramme of cupric sulphate may be taken, dissolved in about 200 c.c. of water and a few drops of hydrochloric acid added. A solution containing equal quantities of ammonium thiocyanate and ammonium (or sodium) bisulphite is then added until no further precipitation takes place. The whole is heated and after the white precipitate of cuprous thiocyanate has settled the clear liquid is poured through a previously weighed filter, the precipitate washed by decantation, transferred to the filter, washed further until no trace of chloride is found in the filtrate, dried in the water-oven (or preferably in an air-bath at a temperature of 110° C.), cooled and weighed.

120·79 grammes of cuprous thiocyanate (CuCNS) represent 63·12 grammes of copper.

The determination of copper as cuprous sulphide involves the use of special apparatus and the ignition of the precipitate with sulphur in an atmosphere of hydrogen.

BISMUTH

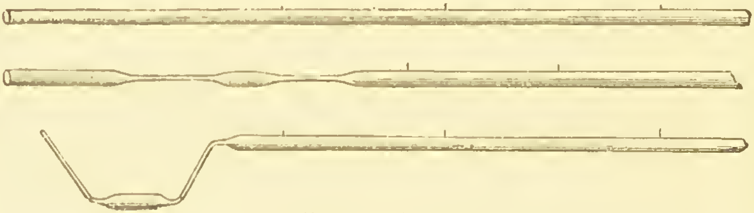
Dissolve 0·3 or 0·4 of the pure bismuth oxycarbonate $(Bi_2O_2CO_3)_2,H_2O$ (*Bismuthi Carbonas*, B.P.) in a very small quantity of hydrochloric acid, dilute with water slightly acidulated with hydrochloric acid, pass excess of hydrogen sulphide through the liquid, collect the precipitate on a tared filter, wash, dry at 212° F. (100° C.), and weigh. The sulphide must not be exposed too long in the water-oven, or it will increase in weight owing to absorption of oxygen; hence it should be tested in the balance every half-hour until it no longer loses weight. 514·85 of oxycarbonate should yield 510·06 of sulphide (Bi_2S_3). The strength of the official solution of bismuth and ammonium citrate (*Liquor Bismuthi et Ammonii Citratis*, B.P.) is determined by this process. "A mixture of 10 cubic centimetres of the solution with 40 cubic centimetres of water, treated with hydrogen sulphide in excess, yields a black precipitate, which, when washed and dried, should weigh at least 0·55 gramme." One fluid drachm yields 3 grains of bismuth oxide.

MERCURY

This element may be (1) isolated and determined in the form of metal, or precipitated and weighed as (2) mercurous chloride, or (3) mercuric sulphide.

Process 1.—The process by which the metal itself is separated is one of distillation into a bulb surrounded by water.

About half a metre of the difficultly fusible German glass known as *combustion-tubing* is sealed at one end after the manner of a test-tube (fig. 56); a mixture of sodium bicarbonate and dry chalk is then dropped into the tube to the height of two or three centimetres, and, next, several small fragments of quicklime so as to occupy another centimetre; a mixture of about a gramme of pure calomel or corrosive sublimate with enough powdered quicklime to occupy 10 or 12 centimetres of the tube is added, then the lime-rinsings of the mixing-mortar, a layer of a few centimetres of powdered quicklime, and, finally, a plug of *asbestos*. The whole should occupy two-thirds of the tube. The part of the tube just above the asbestos is now softened in the blowpipe-flame and drawn out about a decimetre to the diameter of a narrow quill (fig. 57); again drawn out to the same extent at a point two or three centimetres nearer the mouth (fig. 57) and any excess of tubing cut off. The bulb thus formed may be enlarged by softening and blowing. The tube is next softened at a point close to but anterior to the asbestos, and bent to form an obtuse angle; the tube is then softened close to the bulb and slightly bent so that the bulb may be parallel with the long tube; then softened on the other side of the bulb, and the terminal tube bent to an obtuse angle, so that, the tube being held in a horizontal position, the bulb may be sunk in water, and the terminal tube point upwards (fig. 58). The long tube is now laid in the gas-furnace (fig. 59), a basin so placed that the bulb of the apparatus may be cooled by being surrounded by water, the part of the tube occupied by asbestos heated to redness, and the flame



FIGS. 56, 57, 58.

slowly lengthened until the tube is uniformly red-hot. In the circumstances just described the mercury compound is decomposed by the lime and its acid radical fixed, and the mercury carried in vapour to and condensed in the bulb. The carbonic anhydride evolved from the sodium bicarbonate and chalk washes out the last portions of mercury vapour from the tube. When the distillation is considered to be complete, the dish of water is removed, the bulb dried, and then detached by help of a file, at a point beyond any sublimate of mercury. The dried bulb is weighed, the mercury shaken or dissolved out, and the tube again dried and weighed. The difference between the weights gives the weight of the mercury. "Ammoniated Mercury," B.P., should yield 78 to 79 per cent. of metallic mercury.

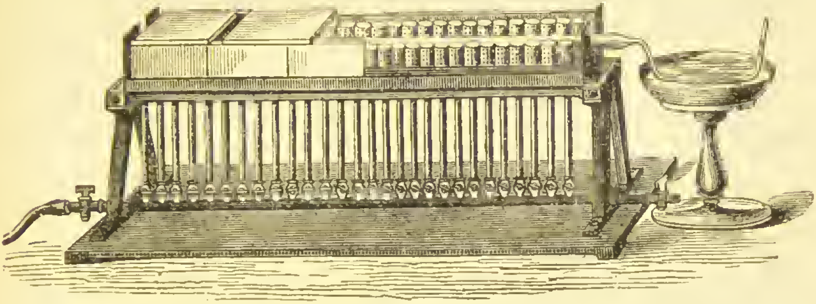


FIG. 59.

Process 2.—The process by which mercury is separated in the form of calomel, consists in adding, *in the cold,* solution of hydrochloric and phosphorous acids to an aqueous or even acid solution of a weighed quantity of the mercurial compound, setting the mixture aside for twelve hours, collecting the precipitate on a tared filter, washing, drying at 212° F. (100° C.), and weighing (Rose). By adding first excess of hydrogen peroxide then phosphorous acid and warming on a water-bath until the precipitate is flocculent the reaction is completed in a few minutes without reduction of calomel to metallic mercury as is the case when the mercuric chloride solution is *heated* with phosphorous acid. The experiment may be tried on about half a gramme of corrosive sublimate.

Process 3.—Two or three decigrammes of corrosive sublimate are dissolved in water, the solution acidulated with hydrochloric acid, excess of hydrogen sulphide passed through it, the precipitate collected on a tared filter, washed with cold water, dried at 212° F. (100° C.), and weighed.

Proportional Weights of Equivalent Quantities of Mercury and its Salts.

Mercury	Hg	198·8
Mercurous chloride	HgCl	233·99
Mercuric chloride	$HgCl_2$	269·18
Mercuric sulphide	HgS	230·62

LEAD

Lead is generally determined either as (1) oxide, (2) sulphate, (3) chromate, or (4) metal.

Process 1.—Weigh out one or two grammes of pure lead acetate in a covered crucible, previously tared, and heat slowly until no more vapours are evolved. Remove the lid, stir down the carbonaceous mass with a clean iron wire, and keep the crucible in the flame so long as any carbon remains unconsumed. Introduce some fragments of fused ammonium nitrate, and again ignite until no metallic lead remains and all excess of the nitrate has been decomposed. Cool and weigh the resulting oxide (PbO).

Process 2.—Dissolve 0·4 or 0·5 gramme of lead acetate in a small quantity of water, drop in dilute sulphuric acid, add to the mixture twice its bulk of alcohol, and set aside. Decant the supernatant liquid, collect the sulphate on a filter, wash with alcohol, dry, transfer to a porcelain crucible, removing as much of the sulphate as possible from the paper, incinerate on the crucible-lid (not in the platinum coil, for the fused particles of reduced lead would alloy with the platinum), ignite, cool, and weigh.

Process 3.—About half a gramme of lead acetate is dissolved in two to three hundred c.c. of water, acetic acid added, and then solution of potassium bichromate. Collect the precipitate on a tared filter, wash, dry at 212° F. (100° C.), and weigh.

Process 4.—In certain cases, notably in that of commercial "white lead," the lead may be determined in the metallic state by means of potassium cyanide. The lead paint (about 20 grammes) is weighed and carefully incinerated. The residue, a mixture of metallic lead and lead oxide, is then mixed with several times its bulk of potassium cyanide, and the whole heated to fusion. With careful manipulation the lead collects in one globule, which, after cooling, may readily be separated from the mixed cyanide and cyanate, and weighed. Commercially pure white lead should yield 74 per cent. of lead.

Volumetric Determination of Lead.

In lead acetate and in the strong solution of lead subacetate the lead may be determined volumetrically by means of normal solution of sulphuric acid. About 3 grammes of lead acetate or from 7 to 10 grammes of the subacetate solution may be used.

$$\underbrace{Pb(C_2H_3O_2)_2,3H_2O}_{2)376\cdot15} + \underbrace{H_2SO_4}_{2)97\cdot34} = PbSO_4 + 2HC_2H_3O_2 + 3H_2O$$

$$\overline{188\cdot075} \qquad \overline{48\cdot67} = \text{grammes in 1000 c.c. of normal solution.}$$

$$\underbrace{Pb_2O(C_2H_3O_2)_2}_{4)543\cdot74} + \underbrace{2H_2SO_4}_{4)194\cdot68} = 2PbSO_4 + 2HC_2H_3O_2 + H_2O$$

$$\overline{135\cdot93} \qquad \overline{48\cdot67} = \text{grammes in 1000 c.c. of normal solution.}$$

The flask in which the operation is being conducted should previously contain one-third of water. In the case of both lead acetate and solution of lead subacetate, a little acetic acid should be added to prevent precipitation of basic salt on dilution. The only indicator of complete reaction is cessation of production of the precipitate—lead sulphate. Both the British and United States Pharmacopœias require lead acetate to be pure (100 per cent.) and strong solution of lead subacetate to contain nearly 25 per cent.

Proportional Weights of Equivalent Quantities of Lead and of some of its Compounds.

Lead	Pb	205·35
Lead acetate	$Pb(C_2H_3O_2)_2,3H_2O$	376·15
Lead oxide	PbO	221·23
Lead sulphate	$PbSO_4$	300·69
Lead chromate	$PbCrO_4$	320·61

SILVER

Silver in compounds which are readily decomposed by heat is determined as (1) metal, in others usually as (2) chloride ($AgCl$), but sometimes as (3) cyanide ($AgCN$).

Process 1.—Heat about a gramme of silver oxide, Ag_2O, in a tared crucible, cool, and weigh. 230·1 of oxide yield 214·22 of metal.

Process 2.—Dissolve 0·4 or 0·5 gramme of pure dry crystals of silver nitrate in water, acidulate with two or three drops of nitric acid, slowly add hydrochloric acid, stirring rapidly, until no more precipitate is produced. Pour off the supernatant liquid through a filter, wash the silver chloride once or twice with hot water, transfer to the filter, complete the washing, and dry. After removing as much as possible of the precipitate from the paper to the crucible, burn the filter, not in a wire helix but on the inverted lid of the crucible, moisten with a drop of nitric acid, warm, add a drop of hydrochloric acid, evaporate to dryness, replace the lid on the crucible, ignite the whole until the edges of the mass of chloride begin to fuse; cool, and weigh. 168·69 of nitrate yield 142·3 of chloride. According to the British Pharmacopœia, 1 part of silver nitrate should yield 0·843 of chloride, and the filtrate from the chloride evaporated to dryness should leave no residue, indicating absence of potassium or sodium nitrates and other similar foreign substances. 3 parts of Mitigated Caustic (*Argenti Nitras Mitigatus*, B.P.), similarly treated, give 0·843 parts of silver chloride, and the filtrate yields potassium nitrate and chloride on evaporation. Toughened Caustic, B.P., contains 5 per cent. of potassium nitrate, hence 1 part will give only 0·8 part of silver chloride, and the filtrate will yield some potassium salt. 10 parts of silver dissolved in nitric acid and treated as above will, if pure, give 13·285 of silver chloride.

Process 3.—Silver cyanide may be collected on a tared filter and dried at 100° C. 168·69 of nitrate yield 132·96 of cyanide.

Silver and its salts may be determined volumetrically by means of a standard solution of sodium chloride.

Cupellation.—The percentage of silver in an alloy may be determined by a dry method. The metal is folded in a piece of thin sheet lead, placed on a *cupel* (*cupella*, little cup, made of compressed bone-earth) and heated in a furnace, the cupel being protected from the direct action of the flame by a case termed a muffle. The metals melt, the baser become oxidised, the lead oxide fusing and dissolving the other oxides; the fluid oxides are absorbed by the porous cupel, a button of pure silver remaining. An alloy suspected to contain 95 per cent. of silver requires about three times its weight of lead for successful cupellation; if 92½ per cent. (English silver coin), between five and six times its weight of lead is necessary.

QUESTIONS AND EXERCISES

Explain the gravimetric process by which the concentration of solutions of ferric chloride, nitrate, and sulphate may be determined.—Mention the various amounts of ferrous and ferric salts equivalent to 100 parts of iron.—State the precautions necessary to be observed in determining arsenium or antimony in the form of sulphide.—In what form are the official compounds of bismuth weighed for quantitative purposes?—Give an outline of the process by which mercury may be isolated from its official preparations and weighed in the metallic condition.—Give three methods for the quantitative analysis of lead salts; and the weights of the respective precipitates, supposing 0·56 grm. of crystallized acetate to have been operated on in each case.—Describe the processes by which silver is determined in the forms of metal, chloride, and cyanide.—What proportions of silver nitrate are indicated, respectively, by 15 of metal, 9·8 of chloride, and 8·1 of cyanide?—Describe cupellation.

DETERMINATION OF ACID RADICALS

CHLORIDES

Free chlorine (chlorine-water) and compounds which by action of acids yield free chlorine (Chlorinated Lime, Chlorinated Soda, and their Solutions) may be determined volumetrically by a standard solution of sodium thiosulphate (*see* p. 742). The quantity of combined chlorine in chlorides may be determined by volumetric analysis with a standard solution of silver nitrate (p. 728).

Combined chlorine is gravimetrically determined in the form of silver chloride, the operation being identical with that described for silver salts (p. 768). 58·07 parts of pure, colourless, crystallized sodium chloride yield 142·3 of silver chloride.

IODIDES

Free iodine is determined volumetrically by means of solution of sodium thiosulphate (*see* p. 743).

Combined iodine is determined gravimetrically in the form of silver iodide, the operations being conducted as with silver chloride. Potassium iodide may be used for an experimental determination : $KI = 164{\cdot}73$ should yield $AgI = 233{\cdot}01$.

Moisture in iodine is roughly determined by loss on exposing a weighed sample on a watch-glass placed in a desiccator over sulphuric acid. Another method consists in adding to a weighed sample five or six times as much mercury, or excess of zinc or silver filings, and a little water, drying and weighing. The weight of the product is the weight of metal employed plus that of the *dry* iodine in the sample.

BROMIDES

Free bromine may be determined by shaking with excess of solution of potassium iodide, and then determining the equivalent quantity of liberated iodine by means of a standard solution of sodium thiosulphate (p. 742).

The bromine in bromides may be precipitated and weighed as silver bromide, the manipulations being the same as those for silver chloride: 0·2 to 0·3 gramme of pure potassium bromide may be used for an experiment.

CYANIDES

Hydrogen cyanide (hydrocyanic acid) is usually determined volumetrically (*see* p. 728).

From all soluble cyanides cyanogen may be precipitated by silver nitrate, after acidulating with nitric acid, the silver cyanide being collected on a tared filter, dried at 100° C., and weighed.

Silver Cyanide.

		In formula wt.	In 100 parts.
Silver	Ag	107·11	80·558
Cyanogen	CN	25·85	19·442
		132·96	100·00

NITRATES

Nitrates cannot be determined by direct gravimetric analysis, none of the metallic radicals yielding a definite nitrate insoluble in water. With some difficulty they may be determined by indirect volumetric methods.

Process.—The following (Thorpe's) method depends upon the fact (Gladstone and Tribe) that when zinc upon which copper is deposited in a spongy form is boiled with water, hydrogen is evolved. Thorpe found that in a solution containing nitrates the nascent hydrogen converts the whole of the nitrogen of the nitrates into ammonia, which may be collected and determined. (The oxygen of the nitrate is simultaneously converted into water, the metallic radical into hydroxide, and the zinc into zinc hydroxide. The power of the copper-zinc couple is considered to depend largely on the hydrogen absorbed by the finely divided metal.)

An apparatus such as shown in fig. 60 should be constructed. A flask (about 100 c.c.) is fitted with a clean sound cork perforated for a delivery-tube, which should be of strong glass tubing of about a quarter-inch bore, and for a stoppered funnel, which should have about half the capacity of the flask. The whole is supported by a clamp or on wire-gauze. The outer jar shown in the figure should have a capacity of two or three litres, and the inner receiving-jar should be capable of holding 200 c.c. The latter is fitted with a cork perforated for the delivery-tube, and perhaps for another tube containing fragments of glass moistened with acidulated water to prevent possible loss of ammonia—though the latter tube is found to be almost unnecessary. The addition of wash-bottle tubes is also recommended as convenient for obtaining the distillate from the jar without dismounting the apparatus from time to time.

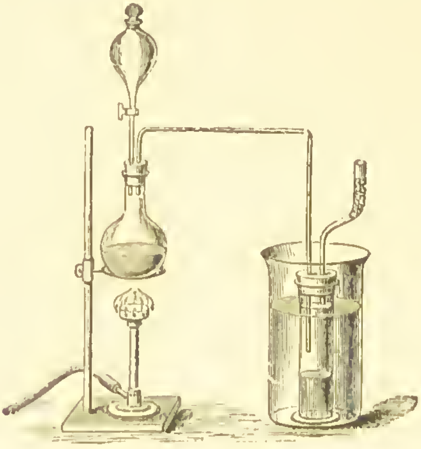


FIG. 60.—Determination of Nitrates.

A few strips of clean zinc (*granulated* zinc recently cleansed with dilute acid is best), are boiled in a beaker with a 3 per cent. solution of cupric sulphate, the operation being repeated with a fresh portion of solution until an adherent and fairly thick coating of finely divided copper is deposited. The pieces of metal are well washed and introduced into the flask, which is then half filled with pure water free from ammonia. To avoid transference, the flask itself may be used instead of the beaker. The funnel also of the apparatus is filled with pure water. Water is now placed around the inner receiver in the outer jar, and, the connections being sound, heat is applied with the view of freeing the apparatus itself from any trace of ammonia. When the contents of the flask are evaporated nearly to dryness, pure water is admitted from the funnel until the flask is again about half full (the funnel should be filled again at once), and the distillation carried on as before. This must be repeated until no further trace of ammonia is evolved, when the apparatus is ready for use. On each occasion that the apparatus is used it must be freed from ammonia in this way. A suitable quantity of the substance to be estimated is now introduced (in the case of potable waters the prepared solid residue from 100 c.c.) and water added, if necessary, until the flask is half full. Heat is now applied and the operation conducted in the manner already described until ammonia no longer comes over—a point which usually occurs in the case of water-residues when the flask has been twice or thrice charged with water and the distillate is about 100 c.c. The warm water from the upper part of the cooling-jar may be removed by a siphon or otherwise, cold water being introduced from time to time.

The ammonia being all evolved, disconnect the flask and receiver simultaneously (unless wash-bottle tubes are fitted), and treat the contents of the latter by the Nessler method described on page 718.——Urea yields but traces of ammonia by this process; and neither the sulphates nor chlorides of the alkali-metals affect the result.——The method is only applicable to highly dilute solutions of nitrates, for with more concentrated solutions oxides of nitrogen are formed and escape.

SULPHIDES

Process.—Soluble sulphides (*e.g.*, H_2S, NaHS) may be determined volumetrically by adding to the aqueous liquid a measured excess of an alkaline arsenious solution of known concentration, neutralizing with hydrochloric acid, diluting to any given volume, filtering off the arsenious sulphide precipitated, taking a portion of the filtrate equal to a half or a third of the original volume, and, after neutralizing with sodium bicarbonate, determining the residual arsenic by means of the standard iodine solution (*see* p. 733).

Process 2.—Sulphur and sulphides may also be quantitatively analysed by oxidizing to sulphuric acid and precipitating in the form of barium sulphate. Thus 2 or 3 decigrammes of a pure metallic sulphide may be decomposed by careful deflagration with a mixture of potassium chlorate and sodium carbonate, the product dissolved in water, acidulated with hydrochloric acid, solution of barium chloride added, and the precipitated barium sulphate washed and collected as described in connection with the estimation of barium (p. 752). Many sulphides may be oxidized by heating in a flask with potassium chlorate and hydrochloric acid, and the sulphate formed is then precipitated by barium chloride. Experimental determinations may also be made on a weighed fragment of sulphur, about 0·1 gramme, cautiously fused with a small quantity of caustic alkali, and the product oxidized while hot by the slow addition of powdered potassium nitrate or chlorate, or, when cold, by treatment with potassium chlorate and hydrochloric acid, the sulphate obtained being subsequently precipitated by barium chloride.

Note.—Fusions performed over a Bunsen flame must be carefully conducted; for any alkali that may creep over the side of a crucible will certainly absorb sulphurous anhydride from the products of combustion of the gas, and error will result.

Process 3.—Soluble sulphides may also be treated with excess of an alkali-metal arsenite, arsenious sulphide then be precipitated by the addition of hydrochloric acid, and the precipitate collected and weighed with the usual precautions (*see* p. 760).

Weights of Equivalent Quantities of Sulphur and of some of its Compounds.

Sulphur	S	31·82
Hydrogen sulphide	H_2S	33·82
Barium sulphate	$BaSO_4$	231·74
Arsenious sulphide	$(As_2S_3) \div 3$	81·49
Iron pyrites	$(FeS_2) \div 2$	59·62
Lead sulphide	PbS	237·17

SULPHITES

Sulphites are usually determined volumetrically by a standard solution of iodine (*see* p. 733). Sulphites insoluble in water are diffused in that menstruum, hydrochloric acid added, and the iodine solution then dropped in.

If necessary, sulphites may be determined gravimetrically by oxidation and precipitation as barium sulphate.

SULPHATES

These salts are always precipitated and weighed as barium sulphate, the manipulations being identical with those performed in the determination of barium by means of sulphates (*see* p. 752). The purity of Sodium Sulphate (*Sodii Sulphas,* B.P.), and the presence of not more than a given quantity of sulphuric acid in vinegar, may be ascertained by this process. Ten grains of sodium sulphate yield 7·23 of barium sulphate. Five ounces of vinegar should yield not more than about $\frac{1}{3}$ gramme of barium sulphate.

Sulphates may be determined volumetrically by a seminormal solution of pure barium chloride, $BaCl_2 2H_2O = 242{\cdot}54$.

The quantity of free sulphuric or hydrochloric acid in vinegar, lemon juice, lime juice, etc., may be ascertained volumetrically by adding a known quantity of standard solution of sodium hydroxide, evaporating to dryness, incinerating, dissolving in water, and by standard acid determining the quantity of sodium hydroxide still remaining free. The caustic soda lost indicates the amount of free mineral acid (Hehner). Thresh first determines the chloride in a sample of vinegar, then adds a known additional amount of chloride, preferably in the form of barium chloride, evaporates, ignites, treats with water, adds sodium bicarbonate to remove excess of barium, filters, and again determines the chlorine. A loss of 70·38 of chlorine (Cl_2) indicates 97·34 of *free* sulphuric acid (H_2SO_4).

The method of determining free sulphuric, nitric, and hydrochloric acids, proposed by Spence and Esilman, is founded on their power of decolorizing a standard solution of ferric acetate.

Proportional Weights of Equivalent Quantities of Sulphates.

The sulphuric radical . .	SO_4 . . .	95·34
Sulphuric acid	H_2SO_4 . . .	97·34
Barium sulphate . . .	$BaSO_4$ . . .	231·74

CARBONATES

Carbonates are usually determined by the loss in weight they undergo on the addition of a strong acid.

Process 1.—A small light flask is selected—of such a size that it can be conveniently weighed in a delicate balance. Two narrow glass tubes are fitted to the flask by means of a cork—the one straight, extending from about two or three centimetres above the cork to the bottom of the flask, the other cut off close to the cork on the inside and curved outwards so as to carry a thin drying-tube horizontally above the flask (*see* fig. 61). The drying-tube is nearly filled with small pieces of calcium chloride, a plug of cotton-wool at either end preventing escape of any fragments, and is attached by means of a pierced cork to the free extremity of the curved tube of the flask. A weighed quantity of any pure soluble carbonate is placed in the flask, a little water added, a miniature test-tube containing sulphuric acid lowered into the flask by means of a thread and supported so that the acid may not flow out, the cork inserted, the outer end of the piece of the straight glass tubing closed by a cap or a fragment of cork, and the whole weighed. The apparatus is then inclined so that the sulphuric acid and carbonate may

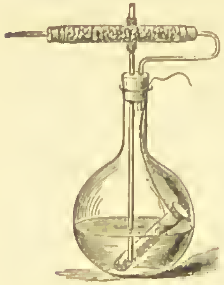


Fig. 61.—Determination of Carbonates.

slowly interact; carbonic anhydride is evolved and escapes through the horizontal tube, any moisture being retained by the calcium chloride. When effervescence has ceased, the gas still remaining in the vessel is sucked out; this is accomplished by fixing a piece of indiarubber tubing to the end of the drying-tube, removing the small plug from the straight tube, and aspirating slowly with the mouth for a few minutes. If the heat produced by the action of the sulphuric acid and solution is considered insufficient to expel all the carbonic anhydride from the liquid, the plug is again inserted in the tube and the contents of the flask gently boiled for some seconds. When the apparatus is nearly cold, more air is again drawn through it, and the whole finally weighed. The loss is due to carbonic anhydride (CO_2), from the weight of which that of any carbonate is ascertained by calculation. Carbonates insoluble in water may be attacked by hydrochloric instead of sulphuric acid; granulated mixtures of carbonates and powdered tartaric or citric acids by enclosing the preparation in the inner tube and placing water in the flask, or *vice versâ*. The apparatus may be modified in many ways to suit the requirements, convenience, or practice of the operator.

Process 2.—Carbonates from which carbonic anhydride is evolved by heat may be determined by the loss they experience on ignition.

Process 3.—Free carbonic anhydride may be absorbed by a solid stick of caustic potash or concentrated alkali solution, the loss in volume of the gas or mixture of gases indicating the quantity originally present.

Weights of Equivalent Quantities of Carbonic anhydride and certain Carbonates.

Carbonic anhydride . . .	CO_2 . . .	43·67
Carbonic acid	H_2CO_3 . . .	61·55
Anhydrous sodium carbonate .	Na_2CO_3 . . .	105·31
Crystalline sodium carbonate .	$Na_2CO_3,10H_2O$.	284·11
Anhydrous potassium carbonate	K_2CO_3 . . .	137·21
Crystalline potassium carbonate	$K_2CO_3 + 16\ \%\ Aq$.	163·34
Calcium carbonate . . .	$CaCO_3$ . . .	99·26

OXALATES

Process 1.—The oxalic radical is usually precipitated in the form of calcium oxalate, and weighed as carbonate, the manipulations being identical with those observed in the determination of calcium (*see* p. 754). The experiment may be performed on 0·3 or 0·4 gramme of pure oxalic acid, 125·1 parts of which should yield 99·26 of calcium carbonate.

Process 2.—Oxalates may also be determined by conversion of their acid radical into carbonic anhydride, and observation of the loss of weight due to escape of the latter. The oxalate, water, and excess of black manganese oxide are placed in the carbonic anhydride apparatus (p. 776), a tube containing sulphuric acid lowered into the flask, the whole weighed, and the operation completed as for carbonates. From the following equation it will be seen that each 87·34 parts of carbonic anhydride evolved indicates the presence of 125·1 parts of crystallized oxalic acid or an equivalent quantity of other oxalate:—

$$Na_2C_2O_4 + MnO_2 + 3H_2SO_4 = MnSO_4 + 2NaHSO_4 + 2H_2O + 2CO_2$$

The black manganese oxide used in this experiment must be free from carbonates. The quantities of the materials employed are regulated by the size of the vessels.

Process 3.—Oxalic acid and oxalates may be determined volumetrically by means of a standard solution of potassium permanganate (*see* p. 740).

PHOSPHATES

Process 1.—*From phosphates soluble in water* the phosphoric radical may be precipitated and weighed in the form of magnesium pyrophosphate, the details of manipulation being similar to those observed in determining magnesium (*see* p. 755). Half a gramme or rather more of pure dry crystallized sodium phosphate may be employed in experimental determinations. The official ammonium phosphate (*Ammonii Phosphas,* B.P.) is quantitatively analyzed by this method. "When 2 grammes are dissolved in water, and solution of magnesium ammonio-sulphate is added in excess, a crystalline precipitate should be formed, which, after being well washed upon a filter with solution of ammonia diluted with an equal volume of water, and then dried, and heated to redness weighs 1·68 grammes." Half a gramme, or less, is a more convenient quantity if the operations be conducted with care. *Solution of magnesium ammonio-sulphate* (B.P.) known as "magnesia mixture," is prepared by dissolving 20 parts of magnesium sulphate, 40 of ammonium chloride, and 84 of solution of ammonia (10 per cent. NH_3) in 160 of distilled water.

Process 2.—*Free phosphoric acid* is most readily determined as lead phosphate $Pb_3(PO_4)_2$. Of the official (B.P.) diluted phosphoric acid it is stated that "each gramme of it mixed with 0·5 gramme of lead oxide in fine powder should leave on evaporation a residue which, after it has been heated to dull redness, weighs 0·6 gramme." The lead oxide must be quite pure; it should be prepared by digesting red lead in warm dilute nitric acid, washing, drying, and heating the resulting puce-coloured lead peroxide in a covered porcelain crucible until it is completely converted into lead oxide (PbO). The increase in weight obtained on evaporating a given quantity of solution of phosphoric acid with a known weight of perfectly pure lead oxide may be regarded as entirely due to phosphoric anhydride (P_2O_5); $3PbO + P_2O_5 = Pb_3(PO_4)_2$, the actual reaction being $3PbO + 2H_3PO_4 = Pb_3(PO_4)_2 + 3H_2O$. From these equations, and the atomic weights (*see* Appendix or Table on p. 52), the percentage of phosphoric acid (H_3PO_4) in any specimen of its solution may easily be calculated.

Process 3.—*The concentration of pure solution of phosphoric acid.* By specific gravity and reference to Tables.

Process 4.—The official *Calcii Phosphas,* and other forms of calcium phosphate known to be tolerably free from iron or aluminium, may be determined by treating about half a gramme with hydrochloric acid somewhat diluted, filtering, if necessary, warming, adding excess of ammonia, collecting the precipitate ($Ca_3(PO_4)_2$), washing, drying, igniting and weighing. The calcium phosphate of pharmacy (*Calcii Phosphas*, B.P.), if pure, will in this process lose little or no weight.

Process 5.—*Insoluble phosphates* in ashes, manures, etc., are treated as follows. The weighed material (1·0 to 10·0 grammes) is digested in hydrochloric acid diluted with three or four times its bulk of water, filtered (insoluble matter and filter being thoroughly exhausted by water), ammonia added to the filtrate and washings, until, after stirring, a faint cloudy precipitate is perceptible, solution of oxalic acid dropped in until, after agitation for a few minutes, the opalescence is destroyed, ammonium oxalate next added, the whole warmed, calcium oxalate removed by filtration, and the filtrate concentrated if very dilute, the liquid treated with citric acid in such quantity that ammonia when added in excess gives a clear *lemon-yellow* solution (Warington), magnesia mixture poured in (as in process 1), and the precipitate of ammonium magnesium phosphate collected, washed, dried, and weighed, as already described in connection with the determination of magnesium.

Relative Weights of Equivalent Quantities of Phosphoric Compounds.

Phosphoric acid . .	H_3PO_4		97·32
Magnesium pyrophosphate	$(Mg_2P_2O_7$	$= 221·12) \div 2 =$	110·56
Lead phosphate . .	$(Pb_3(PO_4)_2$	$= 804·69) \div 2 =$	402·345
Phosphoric anhydride .	$(P_2O_5$	$= 141·0) \div 2 =$	70·5
Calcium phosphate . .	$(Ca_3(PO_4)_2$	$= 307·77) \div 2 =$	153·885
Calcium superphosphate	$(CaH_4(PO_4)_2$	$= 232·35) \div 2 =$	116·175

QUESTIONS AND EXERCISES

What quantity of pure rock-salt is equivalent to 4·2 parts of silver chloride? *Ans.*, 1·71.—State the percentage of real potassium iodide contained in a sample of which 8 parts yield 10·9 of silver iodide. *Ans.*, 96·31.—What is the concentration of a solution of hydrocyanic acid 10 parts of which, by weight, yield 0·9 of silver cyanide? *Ans.*, 1·81 per cent.—How are nitrates quantitatively determined?—By what processes may the quantity of a sulphide present in a solution be determined?—How much real sodium sulphate is contained in a specimen 10 parts of which yield 14·2 of barium sulphate? *Ans.*, 86·46 per cent.—Give details of the operations performed in the quantitative analysis of carbonates.—What weight of carbonic anhydride should be obtained from 10 parts of acid potassium carbonate (or bicarbonate)? *Ans.*, 4·39 parts.—To what operation does the following equation refer, and what are the relative proportions of the reacting substances?

$$Na_2C_2O_4 + MnO_2 + 3H_2SO_4 = MnSO_4 + 2NaHSO_4 + 2H_2O + 2CO_2$$

Explain the lead process for the determination of phosphoric acid in the official solution.—State the quantity of calcium superphosphate equivalent to 7·6 parts of magnesium pyrophosphate. *Ans.*, 7·985 parts.

SILICATES

Silica (SiO_2) may be separated from alkali-metal silicates, or from silicates decomposable by hydrochloric acid, by digesting the substance with hydrochloric acid at a temperature of 70° to 80° C. until completely disintegrated, evaporating to dryness, heating in an air-bath to a temperature of 200° C., again moistening with acid, diluting with hot water, filtering, washing, drying, igniting, and weighing.

DETERMINATION OF WATER

Water and other matters readily volatilized are most usually determined by the loss in weight which a substance undergoes on being heated to a proper temperature. Thus, in the British Pharmacopœia, crystalline gallic acid ($C_7H_6O_5, H_2O$) is stated to lose 9·5 per cent. of its weight when dried at a temperature of 100 °C., cerium oxalate ($Ce_2(C_2O_4)_3,9H_2O$) 53 per cent. on incineration, potassium carbonate about 16 per cent. on exposure to a red heat, quinine sulphate ($[C_{20}H_{24}N_2O_2,H_2SO_4]_2,15H_2O$) 15·2 per cent. at 100° C., and sodium phosphate ($Na_2HPO_4,12H_2O$) 62·84 per cent. at a low red heat; bismuth oxide heated to incipient redness should scarcely diminish in weight.

Process.—One or two grammes of substance is a sufficient quantity in experiments on desiccation, the material being placed in a watch-glass, covered or uncovered porcelain crucible, or other vessel, according to the temperature to which it is to be exposed.

Rapid desiccation at an exact temperature may be effected by introducing the substance into a tube having somewhat the shape of the letter U, sinking the lower part of the tube into a liquid kept at a definite temperature (using a thermometer), and drawing or forcing a current of dry air slowly through the apparatus. Substances liable to oxidation may be desiccated in a current of dried carbonic anhydride. The weights of the U-tube before and after the introduction of the salt, and after desiccation, give the quantity of water sought. In all cases the material must be heated until it no longer loses weight. Occasionally it is desirable to determine water directly by conveying its vapour in a current of air through a weighed tube containing calcium chloride, and re-weighing the tube at the close of the operation; the increase shows the quantity of water.

Note.—Highly dried substances rapidly absorb moisture from the air; they must therefore be weighed quickly, enclosed, if possible, in tubes (p. 747), a light stoppered bottle having a wide mouth, a pair of clamped watch-glasses, or a crucible having a tightly fitting lid.

CARBON, HYDROGEN, OXYGEN, NITROGEN

The quantitative analysis of animal and vegetable substances is either *proximate* or *ultimate*.

Proximate Quantitative Organic Analysis includes the determination of water, oil, albumen, starch, cellulose, gum, resin, alkaloids, acids, glucosides, ash. It requires the application of much theoretical knowledge and manipulative skill, and cannot well be studied except under the guidance of a teacher. One of the best works on the subject is by Rochleder, a translation of whose monographs will be found in the *Pharmaceutical Journal*, vol. i., 2nd ser., pp. 562, 610; vol. ii., 2nd ser., pp. 24, 129, 160, 215, 274, 420, 478. Another is by Prescott, "Outlines of Proximate Organic Analysis." The fullest is by Dragendorff, translated by H. G. Greenish, "Plant Analysis."

Ultimate Quantitative Organic Analysis can only be successfully accomplished with the appliances of a well-appointed laboratory—a good balance, a gas combustion furnace 80 to 90 centimetres long (p. 765), giving a smokeless flame, special forms of glass apparatus, etc. *The theory of the opera-*

tion is simple: a weighed quantity of a substance is completely burned to carbonic anhydride ($CO_2 = 43·67$) and water ($H_2O = 17·88$), and these products are collected separately and weighed; 11·91 parts in every 43·67 of carbonic anhydride are carbon, 2 parts in every 17·88 of water are hydrogen; nitrogen, if present, escapes as gas. If nitrogen be a constituent, it may, in certain cases, be determined by strongly heating a second quantity of the substance with the mixture of sodium and calcium hydroxides known as *soda-lime,* when the nitrogen is converted into ammonia. This ammonia may be determined volumetrically (p. 716) or it may be collected and weighed in the form of ammonium chloroplatinate ($(NH_4)_2PtCl_6 = 440·32$), of which 27·88 parts in every 440·32 are nitrogen. In the case of certain classes of substances containing nitrogen, the *whole* of this element is not convertible into ammonia by heating with soda-line. In these cases the substance is burned under such conditions that its nitrogen is obtained as gas, in which condition it is subsequently measured. The difference between the sum of the weights of hydrogen and carbon, and the weight of substance taken, is the proportion of oxygen in the substance, supposing nitrogen to be absent. If nitrogen is present, the difference between the sum of the percentages of carbon, hydrogen, and nitrogen, and 100, is the percentage of oxygen. Shortly, carbon is determined in the form of carbonic anhydride, hydrogen as water, nitrogen as ammonia, or as nitrogen gas, and oxygen by difference.

The following is an outline of the manipulation necessary for the determination of carbon and hydrogen:—The burning (or *combustion* as it is usually called) of the organic substance is carried out by heating it in a *combustion-tube* of hard glass in a current of air previously freed from water vapour and carbonic anhydride. The combustion-tube has an internal diameter of 15-18 millimetres, and is about 90 centimetres long, being cut to such a length that, when placed in the furnace, it projects about 4-5 centimetres at each side. It is fitted at both ends with perforated indiarubber stoppers, and is packed for about two-thirds of its length with granular cupric oxide, the column of this oxide extending from a little way in front of the middle of the tube to close to the further off end. Prior to carrying out a combustion, the tube with its contents is heated red-hot in the furnace and a current of dried and purified air or oxygen is passed through it, so as to effect the removal of all traces of organic matter from it and from the cupric oxide which it contains. The burners which heat the front (or inlet) portion of the tube are then turned out, and the front half of the tube (embracing the portion which is not packed with cupric oxide) is permitted to cool, without intermission of the air current, while the cupric oxide is maintained at a red heat. The weighed tubes in which the water and the carbonic anhydride are to be separately collected are next attached to the outlet end of the combustion-tube. The *water* is collected in a small U-tube packed with fragments of calcium chloride, or of pumice-stone moistened with concentrated sulphuric acid (fig. 62); the *carbonic anhydride* in a series of bulbs (fig. 62) containing solution of caustic potash (sp. gr. about 1·27). The calcium chloride tube is fitted to the combustion-tube by means of the perforated indiarubber stopper at the outlet end, and the potash-bulbs are attached to the calcium chloride tube by a short piece of indiarubber tubing. The potash-bulbs must carry a short light tube containing a column of small fragments of caustic potash three or four centimetres long: this serves to arrest the small quantity of moisture which is carried away from the solution of potash by the dried air which passes through it during the

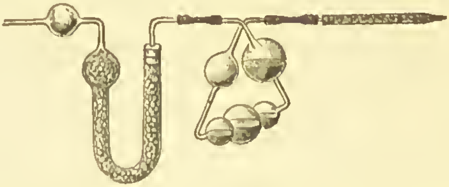


FIG. 62.—Calcium Chloride Tube and Potash-Bulbs.

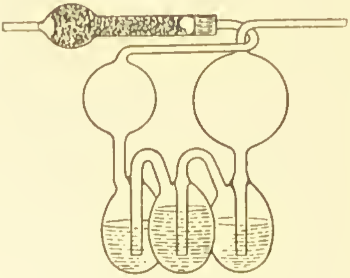


FIG. 63.—Potash-Bulbs.

operation. The form of potash-bulbs illustrated in fig. 62 is that originally introduced by Liebig, but it has now been almost entirely superseded by improved forms. Fig. 63 represents one of the commoner forms now in use.

When the tube has been prepared for the combustion in the manner described, the weighed quantity (usually 0·1 to 0·2 gramme) of the substance to be burned, contained in a porcelain or platinum "boat," is rapidly introduced into the combustion-tube, the stopper at the inlet end being withdrawn for this purpose and then replaced as soon as possible. The substance is now gradually and cautiously heated in the current of air, the furnace burners being lighted at successive intervals of a few minutes, until, eventually, the whole length of the combustion-tube within the furnace is red-hot. The tube is maintained at a red heat, and the current of air (or of oxygen, if necessary) is continued until the substance is completely burned and the products of its combustion have been entirely swept out of the combustion-tube and into the absorption apparatus. The calcium chloride tube and the potash bulbs are detached, and set aside near the balance for some time to cool, and are then separately weighed. The increase in weight of each of the two portions of the absorption apparatus, due to water and to carbonic anhydride respectively, is noted, and the percentages of hydrogen, carbon, and (by difference) oxygen are calculated.

General Manipulation for the Determination of Nitrogen.

1. *Determination by Conversion into Ammonia.*—The combustion-tube employed in this operation is half a metre or more in length, and is drawn out to the diameter of an ordinary quill and closed at one end, the quilled end being about 5 centimetres long, and bent so as to form an obtuse angle with the main portion of the tube. Two such tubes are readily made by softening in the blowpipe-flame two or three centimetres of the central part of a tube about a metre long, and drawing the halves of the tube apart, as shown in

the following engraving (fig. 64). The tubes are separated by melting the glass in the middle of the quilled portion. The soda-lime to be used in converting the nitrogen into ammonia is made by slaking quicklime with a solution containing so much sodium hydroxide that about two parts of quicklime shall be mixed with one of sodium hydroxide, drying the product, heating to bright redness, and finely powdering; it should be preserved in a well-closed bottle. Some of the soda-lime is introduced into the tube, then layers of the weighed substance and soda-lime, thorough mixture of these being effected by means of a long copper wire having a short helix, a good layer of soda-lime is added, and a plug of asbestos. Bulbs (fig. 65), known as those of Will and Varrentrapp (the originators of the method), containing hydrochloric acid of about 25 per cent., are then fitted by means of a cork, and the tube is gradually heated from the outlet end, backwards, to the closed end in the furnace—to a not too bright red heat, or some of the produced ammonia gas may be decomposed. When gas bubbles no longer pass through the bulbs and combustion is considered to be *quite* complete, the tube is allowed to cool somewhat, the quill is then broken, and air is slowly drawn through the tube and bulbs by means of an aspirator until all ammonia gas may be considered to have been absorbed by the acid. The bulbs are disconnected, their contents and rinsings poured into a small dish, solution of chloroplatinic acid added, and the

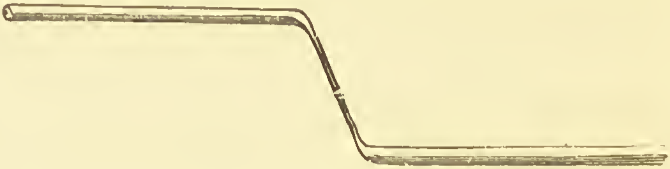


FIG. 64.

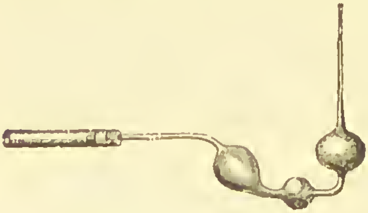


FIG. 65.—Nitrogen-Bulbs.

operation completed as in the determination of potassium and ammonium salts (*see* pp. 749 and 751). Or the ammonia may be absorbed in a known volume of standard sulphuric acid, of which the residual excess is determined by means of a standard alkali; certain obvious calculations then giving the quantity of ammonia produced.

. Conversion into ammonia may also be effected by heating the substance with the most concentrated sulphuric acid and, if not then thoroughly attacked, with potassium permanganate (Kjeldahl).

2. *Determination as Nitrogen Gas* (*Method of Dumas*).—The combustion-tube employed in making nitrogen determinations by this method (which is applicable to all classes of nitrogen compounds) is fitted in the same manner as that used in determining carbon and hydrogen (p. 783), except that the place of 8 to 10 centimetres of the column of cupric oxide, at the outlet end, is taken by a tightly rolled strip of fine copper wire-gauze which accurately fits the tube. The function of this roll of metallic copper is to decompose oxides of nitrogen, which frequently are produced during the combustion, the oxygen combining with the copper while the nitrogen passes on. The combustion is carried out in an atmosphere of carbonic anhydride, and therefore the porcelain boat containing the substance to be burned is placed in position (*i.e.*, in front of the cupric oxide) while the tube is cold, and the whole of the air contained in the tube is displaced by means of a brisk current of pure carbonic anhydride while the cupric oxide is being heated, but before the heating of the substance is begun. When the air has been displaced, the narrow delivery-tube which is fitted into the stopper at the outlet end of the combustion-tube is connected with a nitrometer charged with a concentrated solution of caustic potash. As soon as the cupric oxide and roll of copper gauze are distinctly red-hot, the substance is slowly and cautiously heated, as in the case of a carbon and hydrogen combustion, the whole of the tube within the furnace being raised, eventually, to a moderate red heat. A *very slow*

current of carbonic anhydride is sometimes passed through the tube during the whole combustion. In the case of substances containing a large proportion of carbon, such as alkaloids, it is usually necessary to mix the portion taken for analysis with some finely granular cupric oxide in the porcelain boat, so as to ensure its complete combustion and the evolution of the whole of its nitrogen. When the substance is completely burned, the products of the combustion are slowly driven forward into the nitrometer by passing a moderate current of carbonic anhydride for some time. The carbonic anhydride is absorbed and the water vapour is condensed by the caustic potash solution in the nitrometer, and the nitrogen is collected in a pure state. The volume of the gas and the temperature and pressure at which it was measured are noted and, from the corrected volume, the weight of the nitrogen and the percentage of it present in the substance, are ascertained by making a few simple calculations.

Liquids are analysed by methods similar to those adopted for solids, volatile liquids being enclosed in small bulbs blown on the end of two-inch capillary tubes. These are weighed previously to and after the introduction of the liquid, the end of each capillary tube being sealed prior to the second weighing ; just before being placed in a porcelain boat and introduced into the combustion-tube, the capillary tube is broken.

Limit of experimental errors.—Two determinations of carbon may vary to the extent of 0·1 per cent. ; of hydrogen, 0·2 ; of nitrogen, 0·3.

Chlorine, Bromine, or *Iodine,* contained in an organic substance may be determined by heating with fuming nitric acid and silver nitrate in a sealed tube, or by heating to redness a given weight of the material with ten times as much pure lime in a combustion-tube. By the latter process, calcium chloride, bromide, or iodide is produced. While still hot, the tube is plunged into water, the mixture of broken glass and powder treated with dilute nitric acid in very slight excess ;

the filtered liquid precipitated by the addition of excess of silver nitrate, and the silver chloride, bromide, or iodide collected, washed, dried, cooled, and weighed.

Sulphur, Phosphorus, and *Arsenium* in organic salts may be determined by heating with fuming nitric acid in a sealed tube, or by gradually heating in a combustion-tube 1 part of the substance with a mixture of 10 parts of nitre, 2 of dried sodium carbonate (in order to moderate deflagration), and 20 of sodium chloride. The product is dissolved in water, acidulated by the addition of excess of nitric acid, the sulphuric radical precipitated, and weighed as barium sulphate, the phosphoric and arsenic radicals as ammonium magnesium phosphate and ammonium magnesium arsenate respectively.

QUININE, ETC.

Process of the British Pharmacopœia for ascertaining the amount of Quinine with Cinchonidine, and the amount of Total Alkaloids, in the Succirubra *or Red Cinchona Bark (Cinchonæ Rubræ Cortex,* B.P.).

Mix 20 grammes of Red Cinchona Bark, in No. 60 powder, with 6 grammes of calcium hydroxide; slightly moisten the powders with 20 cubic centimetres of water; mix the whole intimately in a small porcelain dish or mortar; allow the mixture to stand for an hour or two, when it will present the characters of a moist, dark-brown powder, in which there should be no lumps or visible white particles. Transfer this powder to a suitable flask fitted with a small reflux condenser, add 130 cubic centimetres of benzolated amyl alcohol [3 vols. of commercial benzol and one vol. of amyl alcohol], boil them together for about half an hour, decant the liquid on to a filter, leaving the powder in the flask; add more of the benzolated amyl alcohol to the powder, and boil and decant as before; repeat this operation a third time; then turn the contents of the flask on to the filter, and wash by percolation with more of the benzolated amyl alcohol until the Bark is exhausted. Introduce the collected filtrate, while still warm, into a stoppered glass separator; add to it 2 cubic centimetres of diluted hydrochloric acid, mixed with 12 cubic centimetres of water; shake them well together, and when the acid liquid has separated this may be drawn off, and the process repeated with water slightly acidulated with hydrochloric acid, until the whole of the alkaloids have been removed. The liquid should then, while warm, be carefully and exactly neutralized with solution of ammonia, and concentrated to the bulk of 16 cubic centimetres. If now about 1·5 gramme of sodium potassium tartrate, dissolved in twice its weight of water, be added to the solution, and the mixture stirred with a glass rod, insoluble quinine and cinchonidine tartrates will separate completely in about an hour; and these collected on a filter, washed, and dried in a water oven, will contain eight-tenths of their weight of the alkaloids, quinine and cinchonidine, which, multiplied by 5, gives the weight of those alkaloids present in 100 grammes of the Bark. To the mother-liquor from the preceding process add solution of ammonia in slight excess. Collect, wash, and dry the precipitate, which will contain the other alkaloids. The weight of this precipitate multiplied by 5, and added to the percentage weight of the quinine and cinchonidine, gives the percentage weight of total alkaloids.

Note.—If it is desired to obtain each alkaloid separately, the above process may be modified by using dilute sulphuric instead of hydrochloric acid for removing the alkaloids from the benzolated amyl alcohol, and exactly neutralizing with ammonia *while kept hot on a water-bath;* on cooling, the quinine will crystallize out almost completely as neutral sulphate. The cinchonidine may then be precipitated from the filtrate by sodium potassium tartrate, and, after its removal, quinidine, if present, by potassium iodide; finally, cinchonine is obtained by precipitating the filtrate from the quinidine with caustic soda or ammonia.

Extractum Cinchonæ Liquidum, B.P.—The greater portion of the alkaloids of Red Cinchona Bark is dissolved out by water acidulated with hydrochloric acid and containing glycerin. The acid, in acting as a solvent, probably more or less decomposes the natural compounds in the bark. The glycerin contributes to the permanence of the preparation. The mixture is evaporated to a low bulk, assayed as follows, and further evaporated or diluted, until 85 cubic centimetres contain 5 grammes of total alkaloids; 12·5 cubic centimetres of alcohol (90 per cent.) are then added, and the final adjustment of the volume to 100 cubic centimetres effected by the addition of distilled water. The *assay* is thus conducted. Put 5 cubic centimetres of the liquid, together with 25 cubic centimetres of water, into a stoppered glass separator; add 30 cubic centimetres of benzolated amyl alcohol and 15 cubic centimetres of solution of potassium hydroxide, shake them together thoroughly and repeatedly; allow them to remain at rest until the spirituous solution of the alkaloids shall have separated and formed a distinct stratum over the dark-coloured alkaline liquid. Run off the latter by the stopcock into another separator; agitate it thoroughly with 30 cubic centimetres of benzolated amyl alcohol; allow the liquids to separate; draw off and reject the lower layer; add the alcoholic layer to the liquid in the first separator; wash the mixture with a little water; agitate thoroughly with 30 cubic centimetres of a warm mixture of 1 volume of diluted hydrochloric acid and 5 volumes of water; allow the liquids to separate; draw off the lower acid layer into another separator; agitate the alcoholic layer with a second quantity of 30 cubic centimetres of the mixture of water and diluted hydrochloric acid; when separated, draw this off into the other portion of acid liquid; to the mixture add 10 cubic centimetres of chloroform and sufficient solution of ammonia to impart a strongly alkaline reaction; shake thoroughly; allow the liquids to separate; draw off the lower chloroformic layer into a weighed dish; repeat the agitation and separation with two successive quantities of 10 cubic centimetres of chloroform, and add the chloroformic liquids to that in the dish. Allow the chloroform to evaporate slowly; dry the residue in the dish at a temperature of about 230° F. (110° C.). The weight of the dish and its contents, after deduct-ing the known weight of the dish, will give that of the alkaloids.

De Vrij's Method for the Separation of the Mixed Alkaloids from Cinchona Barks. De Vrij's Method for the Separation and Quantitative Determination of all the different Cinchona Alkaloids. For these processes the reader is referred to the eleventh edition of this Manual. *Prollius's Method for the Estimation of Total Alkaloids in Cinchona Bark, as modified by De Vrij.*—See the thirteenth edition.

Official (B.P.) *Methods of Testing Quinine Sulphate for other Alkaloidal Sulphates.*

Test for Cinchonidine and Cinchonine.—Dissolve 4 grammes of the Quinine Sulphate in 120 cubic centimetres of boiling water. Cool the solution slowly to 122° F. (50° C.) with frequent stirring. Separate, by filtration, the purified quinine sulphate which has crystallized out. Concentrate the filtrate by evaporation until it is reduced to 10 cubic centimetres or less; transfer to a small stoppered flask, and, when cold, shake with 10 cubic centimetres of ether and half that volume of solution of ammonia. Set aside in a cool place for not less than 24 hours. Collect the crystals, which consist of cinchonidine and cinchonine combined with quinine, on a tared filter, wash with a little ether, dry at 212° F. (100° C.), and weigh. They should not amount to more than 0·12 gramme.

Test for Quinidine.—Dissolve 1 gramme of the Quinine Sulphate in 30 cubic centimetres of boiling water; cool, and filter. To the solution add solution of potassium iodide, and a little alcohol (90 per cent.) to prevent the precipitation of amorphous hydriodides. Collect any separated quinidine hydriodide, wash with a little water, dry, and weigh. The weight represents about an equal weight of crystallized quinidine sulphate. None, or only the slightest traces should be obtained.

Test for Cupreine.—Shake the recrystallized quinine sulphate, obtained in testing the original Quinine Sulphate for cinchonidine and cinchonine, with 25 cubic centimetres of ether and 6 cubic centimetres of solution of ammonia, and to this ethereal solution, separated, add the ethereal liquid and washings also obtained in testing the original sulphate for the two alkaloids just mentioned. Shake this ethereal liquid with 6 cubic centimetres of a 10 per cent. solution of sodium hydroxide, adding water if any solid matter should separate. Remove the ethereal solution. Wash the aqueous solution with more ether, and remove the ethereal washings. Add diluted sulphuric acid to the aqueous liquid, heated to boiling, until exactly neutral. When cold, collect any crystallized cupreine sulphate on a tared filter, dry, and weigh. None, or only the slightest traces should be obtained.

"Quinine sulphate" should not contain much more than five per cent. of other cinchona alkaloid sulphates.

Quinine sulphate normally contains 15·2 per cent. of water; cinchonidine sulphate 7·0 per cent.; cinchonine sulphate 6·0 per cent.; all given off at 100° to 115° C. The drying should therefore be effected at 120° C., and the dried salt weighed in well-fitting weighing tubes. 100 parts of cinchonidine are equivalent to 116 parts of anhydrous cinchonidine sulphate.

Cinchonidine sulphate is almost the only salt likely to be accidentally present in commercial quinine sulphate, much quinidine being rarely present in bark, and cinchonine sulphate being sufficiently soluble to remain dissolved in the mother-liquors of quinine sulphate. The cinchonidine sulphate may vary from 1 to 18 per cent., but more usually is present to the extent of 4 to 6 per cent.

De Vrij's Chromate Test for the purity of quinine sulphate. —The purity of quinine sulphate may be tested in the following manner (De Vrij):—

Dissolve 1 gramme of the salt in 40 c.c. of hot distilled water and add 6 c.c. of a 5 per cent. solution of pure potassium chromate. Set aside for several hours at a temperature *not above* 15° C., when the quinine will be completely precipitated as chromate. Filter, and, after adding a few more drops of the chromate to the filtrate to make sure that the precipitation has been completed, add 9 or 10 drops of a 5 per cent. solution of caustic soda. If the quinine sulphate was pure, the solution will remain clear, even after a day's standing; but if cinchonidine was present, that alkaloid will be precipitated, and may be filtered off and weighed.

Of the Iron and Quinine Citrate (*Ferri et Quininæ Citras*, B.P.) it is officially stated that 5 grammes dissolved in 45 cubic centimetres of water, and treated with a slight excess of solution of ammonia, give a white precipitate, which, when dissolved out by repeated treatment of the liquid with ether and the latter evaporated and the residue completely dried at 248° F. (120° C.), weighs 0·75 gramme. The precipitate is almost entirely soluble in a small quantity of purified ether; when burned, it leaves but a minute residue; neutralized with sulphuric acid, it should answer to the characters of and tests for Quinine Sulphate.

A Process for the Determination of the Quinine of the Scale Compound.—To the residue obtained as stated in the foregoing paragraph, about 25 c.c. of water and enough dilute sulphuric acid to impart a decidedly acid reaction are added. The mixture is next heated over a water-bath until, the solution remaining acid, the residue has completely dissolved. Dilute solution of caustic soda is afterwards added with great care until the solution is exactly neutral. The dish is then removed and the solution allowed to cool and rest over night, when the quinine will have separated in crystals of ordinary sulphate. These should be collected on a filter, and the mother-liquor tested with litmus-paper. If it is acid, it must be warmed over a water-bath and dilute soda solution added to exact neutralization, and the solution set aside as before, when some more crystals will probably separate. These also are collected and with the former ones washed, dried at 120° C., and weighed [$(C_{20}H_{24}N_2O_2)_2,H_2SO_4 = 741{\cdot}02$]. To this weight must be added 1 gramme for every 750 c.c. of mother-liquor on account of the quinine sulphate which it retains in solution. From this weight of anhydrous quinine sulphate is calculated its equivalent of hydrous quinine $(C_{20}H_{24}N_2O_2)_2$, $2H_2O = 679{\cdot}44$, the approximate formula of hydrous quinine dried over a water-bath. The weight thus obtained is compared with the weight of total alkaloid determined, both having been reduced to percentages. The quantity of hydrous quinine calculated from the crystals of sulphate should not be much below that weighed directly. In good specimens the difference will be about one per cent.

Quinine sulphate should yield, according to De Vrij, at least 91·6 per cent. of quinine tartrate.

MORPHINE

The official (B.P., 1898) *process for the estimation of this alkaloid in opium* is the Hager-Jacobsen method somewhat modified, and is conducted in the following manner:—

Test.—Take of opium, dried at 212° F. (100° C.), and in No. 50 powder, 14 grammes; calcium hydroxide, freshly prepared 6 grammes; ammonium chloride 4 grammes; alcohol (90 per cent.), ether, distilled water, of each a sufficiency. Triturate together the opium, calcium hydroxide, and 40 cubic centimetres of water in a mortar until a uniform mixture results; add 100 cubic centimetres of water, and stir occasionally during half an hour. Filter the mixture through a plaited filter about 10 centimetres in diameter into a wide-mouthed bottle having a capacity of about 300 cubic centimetres and marked at exactly 104 cubic centimetres, until the filtrate reaches this mark. To the filtered liquid (representing 10 grammes of opium) add 10 cubic centimetres of alcohol (90 per cent.) and 50 cubic centimetres of ether; shake the mixture; add the ammonium chloride, shake well and frequently during half an hour, set aside for twelve hours for the morphine to separate. Counterbalance two small filters; place one within the other in a small funnel in such a way that the triple fold of the inner filter shall be superposed upon the single fold of the outer filter; wet them with ether; remove the ethereal layer as completely as possible by means of a small pipette, transferring the liquid to the filter; rinse the bottle with 20 cubic centimetres of ether, again transferring the ethereal layer, by means of the pipette, to the filter; wash the filter with a total of 10 cubic centimetres of ether, added slowly and in portions. Let the filter dry in the air, and pour upon it the contents of the bottle in portions, in such a way as to transfer the granular crystalline morphine as completely as possible to the filter. When all the liquid has passed through, wash the remainder of the morphine from the bottle with morphinated water * until the whole has been removed. Wash the crystals with morphinated water until the washings are free from colour ; allow the filter to drain, and dry it, first by pressing between sheets of bibulous paper, afterwards at a temperature between 131° and 140° F. (55° and 60° C.), finally at 230° F. (110° C.) for 2 hours. Weigh the crystals in the inner filter, counterbalancing by the outer filter. Take 0·5 gramme of the crystals and titrate with decinormal volumetric solution of sulphuric acid until the liquid, after boiling, slightly reddens blue litmus paper. 1 cubic centimetre of this volumetric solution represents 0·0283 gramme of pure anhydrous morphine. The weight of pure anhydrous morphine indicated by the titration as obtainable from the total quantity of the crystals, plus 0·101 gramme (representing the average loss of morphine during the process), should amount in total to 1 gramme; that is to say, to a total of not less than 0·95 gramme and not more than 1·05 grammes, corresponding to about 10 per cent. of anhydrous morphine in the dry powdered opium.

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* *Morphinated Water.*—"Prepared by digesting pure morphine in Chloroform Water for seven days at a temperature of 60° F. (15·5° C.), with occasional agitation, so as to obtain a saturated solution of the alkaloid, and filtering from the undissolved morphine." Morphine is "the precipitate obtained on adding solution of ammonia, in slight excess, to a solution of a pure morphine salt in water, the precipitate being washed with water until free from ammonium salt." B.P.

Teschemacher and Smith's Method.—Thoroughly exhaust 200 grains of opium with warm distilled water. Concentrate this watery extract to a thin syrup in a shallow dish, over a water-bath, the water of which should not quite boil. Transfer this thin syrup to a suitable flask, which permits the use of a soft cork, using a few drops of water successively, to wash out the dish. Add to the contents of the flask 50 fluid grains of alcohol, sp. gr. about 0·820, and about 600 fluid grains of ether. Mix gently, but thoroughly, and then add some 50 fluid grains of ammonia, sp. gr. 0·935. Shake the contents of the flask well to precipitate the alkaloids in arenaceous crystals, with occasional agitation during the ensuing eighteen hours. Transfer the contents of the flask to a vacuum filter, and permit all the adherent liquid to be drawn away, washing out the flask with morphinated spirit,* and continue its use till the liquid passes colourless. Then wash with morphinated water, till this also passes colourless. Now dry, slowly at first, finishing at 212° F. Transfer the dried substance to a mortar, reduce it to a very fine powder, and digest it thoroughly in benzene to dissolve the narcotine and such of the opium alkaloids other than morphine, as may be present. Transfer this mixture to a vacuum filter, wash out the mortar carefully with benzene, which use to wash the powder thoroughly. The latter consists of morphine, free from other opium alkaloids and narcotine, but still containing colouring and possibly other organic matters to the extent of 3 to 10 per cent. Dry and weigh this powder. Now ascertain the percentage by weight of crystallized morphine by titration of this powder with standard hydrochloric acid, using litmus as the indicator. (This acid is so made that 1000 grains by weight shall exactly neutralize 100 grains of pure morphine crystallized from water, washed with ether, and gently dried finally at 212° F.)

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* *Morphinated Spirit.*—Digest a large excess of morphine in rectified spirit of 80 per cent., for several days, with frequent agitation. Filter for use.

Of Morphine Hydrochloride it is officially stated that 2 grammes, "dissolved in 250 cubic centimetres of warm morphinated water, with solution of ammonia added in the slightest possible excess, will give on cooling a crystalline precipitate which, when washed with a little cold morphinated water and dried, should weigh 1·51 grammes. The drying should be accomplished, first by pressing the precipitate between sheets of bibulous paper, then by exposing it to a temperature between 131° and 140° F. (55° and 60° C.), and finally to a temperature of 230° F. (110° C.) for twenty minutes." The acetate (*Morphinæ Acetas*, B.P.) is liable to lose acetic acid and become basic, hence the following official requirements: "2 grammes of the salt form with 6 cubic centimetres of warm morphinated water a slightly turbid solution, which is rendered clear by the addition of 0·1 cubic centimetre of acetic acid; and this solution, when mixed with solution of ammonia in slight excess, yields a precipitate which, after washing and drying as described under 'Morphinæ Hydrochloridum,' weighs 1·42 grammes. If the salt yield a larger proportion of morphine than this, it should be recrystallized from hot water acidulated with acetic acid."

NUX-VOMICA ALKALOIDS

The British Pharmacopœia directs that its three galenical preparations of nux vomica (*Extractum Nucis Vomicæ Liquidum*, *Extractum Nucis Vomicæ*, and *Tinctura Nucis Vomicæ*) shall contain defined proportions of the chief alkaloid of the drug. ——The *Liquid Extract* is made by exhausting powdered nux vomica with alcohol (70 per cent.) by percolation. The proportion of strychnine in the resulting strong liquid extract is determined by the following official analytical process:—Evaporate 10 cubic centimetres to a thick syrupy consistence on a water-bath; dissolve the residue in 20 cubic centimetres of water, heating if necessary; place the solution in a separator, and add 5 grammes of sodium carbonate dissolved in 25 cubic centimetres of water, together with 10 cubic centimetres of chloroform; agitate thoroughly; set aside; separate the clear chloroformic solution. Twice repeat the agitation with chloroform, and the separation. Mix 6 cubic centimetres of diluted sulphuric acid with 25 cubic centimetres of water; divide this into three parts, and shake the mixed chloroformic solutions with each in turn. Dilute the united acid liquids with water to 175 cubic centimetres; transfer to a stoppered flask, adding 25 cubic centimetres of solution of potassium ferrocyanide; shake well and frequently during half an hour; allow to stand for six hours. Transfer the precipitate to a small filter, rinsing out the last portions with water containing one-fortieth of its volume of diluted sulphuric acid, and wash until the washings are free from bitterness. Rinse the precipitate into a separator. Add 5 cubic centimetres of solution of ammonia, and shake well; then add 15 cubic centimetres of chloroform in two successive portions, shaking well after each addition; separate the chloroformic solutions, mix and allow the chloroform to evaporate in a counterpoised dish in a current of warm air; dry the residue for one hour on a water-bath, covering the dish to avoid loss of strychnine from decrepitation; weigh.

From this weight calculate the amount of strychnine in the strong liquid extract, and add to the latter sufficient alcohol (70 per cent.) to produce a liquid extract of nux vomica containing 1·5 grammes of strychnine in 100 cubic centimetres, or $1\frac{1}{2}$ grains in 110 minims.

The *Extract* is prepared by adding so much milk-sugar to the evaporated liquid extract, that 5 per cent. of strychnine shall be present; the *Tincture* (0·25 grm. per 100 c.c.) by adding distilled water and alcohol to the liquid extract.

SUGAR

The qualitative test for sugar, by means of an alkaline cupric solution (*see* p. 560), may be applied in the determination of sugar in saccharine substances.

Process.—34·65 grammes of pure dry crystals of ordinary cupric sulphate are dissolved in about 250 c.c. of distilled water. 173 grammes of pure crystals of potassium sodium tartrate are dissolved in 480 c.c. of solution of caustic soda of sp. gr. 1·14. The solutions are *only mixed when required,* water being then added to form 1 litre; smaller quantities of the fluids being proportionately diluted. 100 c.c. of this mixture represent 3·465 grammes of cupric sulphate, and correspond to 0·500 gramme of pure anhydrous grape-sugar, 0·475 of cane-sugar, 0·807 of maltose, or 0·450 of starch. The solutions must be preserved in well-stoppered bottles to prevent absorption of carbonic anhydride, and should be kept in a dark place. Should the mixture give a precipitate on boiling, a few drops of caustic soda may be added when making experiments. Such a reagent is known as *Fehling's solution.*

Dissolve 0·475 grm. of pure powdered cane-sugar in about 50 c.c. of water, convert into inverted sugar by acidulating with sulphuric acid and heating for a hour or two on a water-bath, make slightly alkaline with sodium carbonate, and dilute to 100 c.c. Place 10 c.c. of the cupric solution in a small flask, dilute with three or four times its volume of water, and gently boil. Into the boiling liquid drop the solution of sugar from a burette, 1 cubic centimetre, or less, at a time, until, after standing for the precipitate to subside, the supernatant liquid has just lost its blue colour; 10 c.c. of the solution of sugar should be required to produce this effect—equivalent to 0·0475 of cane-sugar, 0·0807 of maltose, or 0·0500 of grape-sugar. Experiments on pure cane-sugar must be practised until accuracy is attained; syrups, diabetic urine, and saccharated substances containing unknown quantities of sugar may then be analysed.

Starch is converted into grape-sugar by gentle ebullition with dilute acid for eight or ten hours, the solution being finally diluted so that sugar corresponding to one part of starch shall be contained in about 150 of water.

If, instead of Fehling's solution, Pavy's ammoniated solution be used (*Proceedings of the Royal Society*, vol. xxviii., p. 260; and vol. xxix., p. 272; or *Lancet*, March 1, 1884, p. 376; or *Pharmaceutical Journal*, 3 ser., vol. xvii., p. 856), one-fifth more of the cupric salt will be required for the same quantity of sugar.

In cases in which loss of blue colour cannot be relied on as indicating the termination of the reaction, the cuprous oxide should be rapidly filtered out, washed, dried, and ignited, the filter being ignited separately, to minimise the risk of reduction, and its ash added, and the resulting black cupric oxide weighed. When the highest attainable degree of accuracy is required, it is now customary to determine the quantity of copper contained in the precipitated cuprous oxide by depositing it electrolytically and weighing it. One gramme of cupric oxide (or of cuprous oxide or of metallic copper) indicates the subjoined amounts of the respective sugars.

One gramme of	Glucose.	Cane-sugar.	Milk-sugar.	Malt-sugar.
Cupric oxide	·4535	·4308	·6153	·7314
Cuprous oxide	·5042	·4790	·6843	·8132
Metallic copper	·5634	·5395	·7707	·9089

Sugar may be estimated roughly by the measurement of the carbonic anhydride evolved, or of the alcohol produced, during fermentation with yeast. In the method of Einhorn, a measured quantity of urine is shaken up with purified yeast and the mixture is introduced into a tube shaped like the Doremus Ureometer figured on p. 678 which is then allowed to stand at the ordinary temperature for twenty-four hours. From the volume of carbonic anhydride evolved during the fermentation the quantity of sugar is calculated, or the tube may be so graduated as to indicate the percentage of sugar in the urine. Should the urine contain more than 1 per cent. of sugar, it must be diluted and the experiment repeated.

Saccharimetry.—A generic term for certain quantitative operations, undertaken with the view of ascertaining the quantity of sugar present in any matter in which it may be contained.

Saccharimetry is frequently performed upon common syrup (*Syrupus,* B.P.) and solutions which are known to contain nothing but ordinary cane-sugar, the object being merely to ascertain the quantity present. In such a case, it is only necessary to take the specific gravity of the liquid at 60° F. (15·5° C.), and then refer to a previously prepared Table of densities and percentages.

Specific gravity.	Cane-sugar, per cent.	Specific gravity.	Cane-sugar, per cent.	Specific gravity.	Cane-sugar, per cent.
1·007	1·8	1·100	23·7	1·210	45·8
1·014	3·6	1·108	25·4	1·221	47·8
1·022	5·6	1·116	27·1	1·231	49·7
1·029	7·3	1·125	29·0	1·242	51·7
1·036	9·0	1·134	30·9	1·252	53·4
1·044	10·9	1·143	32·8	1·261	55·0
1·052	12·8	1·152	34·6	1·275	57·4
1·060	14·7	1·161	36·4	1·286	59·3
1·067	16·3	1·171	38·4	1·298	61·4
1·075	18·1	1·180	40·1	1·309	63·2
1·083	19·9	1·190	42·0	1·321	65·2
1·091	21·7	1·199	43·7	1·330(B.P.)	66·6

The specific gravity may be taken by means of a hydrometer, technically termed a *saccharometer.* (The specific gravities above correspond to the degrees of Baumé's Hydrometer from 1° to 36°.)

If a liquid contains other substances besides cane-sugar, the test of specific gravity is of little or no value. Advantage may then frequently be taken of the fact that a solution of cane-sugar causes rotation of the plane of polarization of a ray of plane-polarized light to the right, to an extent proportionate to the quantity of sugar in solution. The saccharine fluid is placed in a long tube having opaque sides and transparent ends; and a ray of homogeneous light, polarized by reflection from a black-glass mirror or otherwise, is sent through the liquid and optically examined by the aid of a plate of tourmaline, Nicol's prism, or other polarizing eyepiece. Attached to the eyepiece is a short arm which traverses a circle divided into degrees. The eyepiece and arm are previously so adjusted that when the polarized ray is no longer visible the arm points to the zero of the scale of degrees. The saccharine solution, however, so rotates the plane of polarization of the ray as to again render it visible; and the number of degrees through which the eyepiece has to be rotated before the ray is once more invisible is proportional to the quantity of sugar in the solution. The value of the degrees having been ascertained by direct experiment, and the results tabulated, a reference to the table indicates the percentage of sugar in the liquid under examination. Grape-sugar is dextro-rotatory, but less powerfully than cane-sugar; moreover, grape-sugar, unlike cane-sugar, does not suffer inversion (*see* p. 560) on the addition of hydrochloric acid to its solution—an operation that furnishes data for ascertaining the quantities of cane- and of grape-sugar, or of crystallizable and non-crystallizable sugar, present in a mixture. In using the polariscope in saccharimetry, it is convenient to employ tubes of uniform size, and always to operate at the same temperature. Various modes are adopted of applying for quantitative purposes this action of cane-sugar and other varieties of sugar on polarized light.

ALCOHOL

Mulder's process for the approximate determination of the quantity of alcohol in wine, beers, tinctures, and other alcoholic liquids containing vegetable matter, is as follows:—Take the specific gravity and temperature of the liquid, and measure off a certain quantity (100 cubic centimetres); evaporate to one-half or less, avoiding ebullition in order that particles of the material may not be carried away by the steam. Dilute with water to the original volume, and take the specific gravity at the same temperature as before. Of the figures representing the latter specific gravity, all over 1·000 show to what extent dissolved solid matter affected the original specific gravity of the liquid. Thus, the specific gravity of a sample of wine at 15·5° C. is 0·9951 ; evaporated till all alcohol is removed, and then diluted with water to the original volume, the specific gravity at 15·5° C. is 1·0081 ; and 1·0081 − 1·000 = 0·0081, which latter figure represents the effect of the dissolved solid matter in 0·9951 part of the original wine. 0·0081 subtracted from 0·9951 leaves 0·987, which is the specific gravity of the alcohol and water of the wine. Or, divide the specific gravity of the wine by the specific gravity of the wine minus alcohol, carrying out the division to four places of decimals ; the quotient shows the specific gravity of the water and alcohol only of the wine. On referring to a table of the strengths of diluted alcohol of different specific gravities, 0·987 at 15·5° C. is found to indicate a spirit containing 8 per cent. of alcohol. If the removal of the alcohol from the wine be conducted in a retort, the liquid being boiled and the steam carefully condensed ; and the distillate be diluted with water to the original volume of the wine operated on, the resulting mixture will furnish a liquid which still more accurately represents the original wine in the proportion of alcohol which it contains. The number in the table corresponding to the specific gravity of this liquid then shows the percentage of alcohol present in the wine.

DIALYSIS

Dialysis (from διὰ, *dia,* through, and λύσις, *lusis,* a loosing or resolving) is a term applied by Graham to a process of analysis by diffusion through a porous septum. The apparatus used in the process is called a *dialyzer,* and is constructed and employed in the following manner. The most convenient septum is the commercial article known as *parchment paper,* made by immersing unsized paper for a short time in sulphuric acid and then thoroughly washing it in water. A piece of this material is stretched over a gutta percha hoop, and secured by a second external hoop. Dialyzers of useful size are one or two inches deep and five to ten inches wide. Liquids to be dialyzed are poured into the dialyzer, which is then floated in a flat dish containing distilled water. The portion passing through the septum is termed the *diffusate,* the portion which does not pass through is termed the *dialysate.*

The practical value of dialysis depends upon the fact that certain substances diffuse through a given porous septum far more rapidly than others. Uncrystallizable substances diffuse very slowly. Of such substances as starch, gum, albumen and gelatin, the last named is one of those which diffuse most slowly; hence substances of this class are termed *colloids,* or bodies like *collin,* which is the soluble form of gelatin. Substances which diffuse rapidly are mostly crystalline; hence bodies of this class are termed *crystalloids.*

By the aid of dialysis it is possible to separate small quantities of crystalloid substances from the large quantities of colloid matter often present in vegetable and animal liquids.

QUESTIONS AND EXERCISES

Potassium carbonate is said to lose 16 per cent. of water on exposure to a red heat; give the details of manipulation observed in verifying this statement.—Write a few paragraphs descriptive of the process of ultimate organic analysis.—In what forms are carbon, hydrogen, and nitrogen weighed in quantitative organic analysis?—In the combustion of 0·41 gramme of sugar, what weights of products will be obtained? *Ans.*, 0·632 gramme of carbonic anhydride (CO_2) and 0·237 gramme of water (H_2O).—How is cinchona bark assayed for mixed alkaloids?—Give the official method for the estimation of morphine in opium.—Mention the operations necessary for the determination of the proportion of sugar in saccharated iron carbonate, or in a specimen of diabetic urine.—What is understood by *saccharimetry?*—Give two processes for the estimation of the percentage of alcohol in tinctures, wines, or beer.—Define dialysis.

CONCLUSION

Detailed instructions for the quantitative analysis of potable water, articles of food, general technical products, special minerals, soils, manures, air, illuminating agents (including solid fats, oils, spirits, petroleum, and gas), dyes, and tanning materials, would scarcely be in place in this volume.

The course through which the reader has been conducted will, it is hoped, have taught him the principles of the science of chemistry, and have given him special knowledge concerning the applications of that science to medicine and pharmacy, as well as have imparted sufficient manipulative skill to meet the requirements of manufacture or analysis. The author would venture to suggest that this knowledge be utilized, not only in the way of personal advantage, but in experimental researches on chemical subjects connected with pharmacognosy, pharmacology, therapeutics, and pharmacy. The discovery and publication of a new truth, great or small, is the best means whereby to aid in advancing the calling in which we may be engaged, increase our own reputation, and contribute to that "ultimate end of knowledge" which Bacon described as "employing the Divine gift of reason to the use and benefit of mankind."

NEUTRALIZATION TABLES.

Equivalent weights of Citric Acid, Tartaric Acid, Potassium Carbonate, Potassium Bicarbonate, Sodium Carbonate, Sodium Bicarbonate, Ammonium Carbonate, and Magnesium Carbonate; repeated (in black) for 20 parts of each, and incidentally (in roman) for other proportions. (Exact to two places of decimals.)

Citric Acid $H_3C_6H_5O_7$, $H_2O \div 3 \times 2 = 139$	20·00	18·66	17·02	13·99	9·78	16·66	26·72	29·21
Tartaric Acid $H_2C_4H_4O_6 = 148{\cdot}92$	21·43	20·00	18·23	14·98	10·48	17·85	28·63	31·30
Potassium Carbonate $K_2CO_3 + 16\ \%\ Aq = 163{\cdot}345$	23·50	21·93	20·00	16·43	11·50	19·51	31·41	34·33
Potassium Bicarbonate $2KHCO_3 = 198{\cdot}76$	28·60	26·69	24·34	20·00	14·00	23·82	38·22	41·77
Sodium Carbonate Na_2CO_3, $10H_2O = 284{\cdot}11$	40·88	38·16	34·79	28·59	20·00	34·05	54·63	59·77
Sodium Bicarbonate $2NaHCO_3 = 166{\cdot}86$	24·01	22·41	20·43	16·79	11·75	20·00	32·08	35·07
Ammonium Carbonate $N_3H_{11}C_2O_5 \div 3 \times 2 = 104{\cdot}02$	14·97	13·97	12·74	10·47	7·32	12·47	20·00	21·86
Magnesium Carb. $3MgCO_3$, $Mg(OH)_2$, $4H_2O \div 4 = 95{\cdot}16$	13·69	12·78	11·65	9·57	6·70	11·40	18·30	20·00

The quantity of each acid given in any column neutralizes the quantity of each carbonate in the same column, and *vice versâ*.
Lemon-Juice (sp. gr. 1·030 to 1·040) contains, on an average, 7¾ per cent. by weight of citric acid.

The same Table, in round numbers, for purposes of prescribing and dispensing.

Citric Acid	20	19	17	14	10	17	27	29
Tartaric Acid	21	20	18	15	10	18	29	31
Potassium Carbonate (Potassii Carbonas, B.P.)	23	22	20	16	11	20	31	34
Potassium Bicarbonate (Potassii Bicarbonas, B.P.)	29	27	24	20	14	24	38	42
Sodium Carbonate (cryst.) (Sodii Carbonas, B.P.)	41	38	35	29	20	34	55	60
Sodium Bicarbonate (Sodii Bicarbonas, B.P.)	24	22	20	17	12	20	32	35
Ammonium Carbonate (Ammonii Carbonas, B.P.)	15	14	13	10	7	12	20	22
Magnesium Carbonate (Magnesii Carbonas, B.P.)	14	13	12	10	7	11	18	20

The Table is read thus: 20 grains of Citric Acid will neutralize 29 grains of Potassium Bicarbonate; 20 grains of Sodium Bicarbonate will neutralize or be neutralized by 18 grains of Tartaric Acid; 10 grains of Tartaric Acid will neutralize or be neutralized by 7 grains of Ammonium Carbonate; 20 grains of Sodium Bicarbonate are equivalent to, or will neutralize as much acid as, 34 grains of Sodium Carbonate; 14 grains of Citric Acid are equivalent in neutralizing power to 15 of Tartaric Acid. It is occasionally convenient to double the numbers, halve them, or take some other proportion; also to employ them in weights other than grains.

Lemon-Juice contains, on an average, 35 grains of Citric Acid in 1 fluid ounce.

THE ELEMENTS

Names.	Symbols.	B.P. Atomic Weights. H = 1	International Atomic Weights.	
			O = 16	H = 1
Aluminium	Al	**26·90**	27·1	26·9
Antimony	Sb	**119·00**	120·2	119·3
Argon	A	...	39·9	39·6
Arsenium	As	**74·50**	75·0	74·4
Barium	Ba	**136·40**	137·4	136·4
Bismuth	Bi	**207·30**	208·5	206·9
Boron	B	**10·85**	11	10·9
Bromine	Br	**79·35**	79·96	79·36
Cadmium	Cd	...	112·4	111·6
Cæsium	Cs	...	133	132
Calcium	Ca	**39·71**	40·1	39·8
Carbon	C	**11·91**	12·00	11·91
Cerium	Ce	**139·20**	140	139
Chlorine	Cl	**35·19**	35·45	35·18
Chromium	Cr	**51·74**	52·1	51·7
Cobalt	Co	...	59·0	58·56
Columbium (Niobium)	Cb	...	94	93·3
Copper	Cu	**63·12**	63·6	63·1
Erbium	E	...	166	164·8
Fluorine	F	...	19	18·9
Gadolinium	Gd	...	156	155
Gallium	Ga	...	70	69·5
Germanium	Ge	...	72·5	71·9
Glucinum (Beryllium)	Gl	...	9·1	9·03
Gold	Au	**195·70**	197·2	195·7
Helium	He	...	4	4
Hydrogen	H	**1·00**	1·008	1·000
Indium	In	...	114	113·1
Iodine	I	**125·90**	126·85	125·90
Iridium	Ir	...	193·0	191·5
Iron	Fe	**55·60**	55·9	55·5
Krypton	Kr	...	81·8	81·2
Lanthanum	La	...	138·9	137·9
Lead	Pb	**205·35**	206·9	205·35
Lithium	Li	**6·97**	7·03	6·98
Magnesium	Mg	**24·18**	24·36	24·18
Manganese	Mn	**54·52**	55·0	54·6
Mercury	Hg	**198·80**	200·0	198·5
Molybdenum	Mo	...	96·0	95·3

THE ELEMENTS—*continued*

Names.	Symbols.	B.P. Atomic Weights. H = 1	International Atomic Weights.	
			O = 16	H = 1
Neodymium	Nd	...	143·6	142·5
Neon	Ne	...	20	19·9
Nickel	Ni	...	58·7	58·3
Nitrogen	N	**13·94**	14·04	13·93
Osmium	Os	...	191	189·6
Oxygen	O	**15·88**	16·00	15·88
Palladium	Pd	...	106·5	105·7
Phosphorus	P	**30·80**	31·0	30·77
Platinum	Pt	**193·30**	194·8	193·3
Potassium	K	**38·83**	39·15	38·86
Praseodymium	Pr	...	140·5	139·4
Radium	Ra	...	225	223·3
Rhodium	Rh	...	103·0	102·2
Rubidium	Rb	...	85·4	84·8
Ruthenium	Ru	...	101·7	100·9
Samarium	Sm	...	150	148·9
Scandium	Sc	...	44·1	43·8
Selenium	Se	...	79·2	78·6
Silicon	Si	...	28·4	28·2
Silver	Ag	**107·11**	107·93	107·12
Sodium	Na	**22·88**	23·05	22·88
Strontium	Sr	...	87·6	86·94
Sulphur	S	**31·82**	32·06	31·83
Tantalum	Ta	...	183	181·6
Tellurium	Te	...	127·6	126·6
Terbium	Tb	...	160	158·8
Thallium	Tl	...	204·1	202·6
Thorium	Th	...	232·5	230·8
Thulium	Tm	...	171	169·7
Tin	Sn	**118·20**	119·0	118·1
Titanium	Ti	...	48·1	47·7
Tungsten	W	...	184·0	182·6
Uranium	U	...	238·5	236·7
Vanadium	V	...	51·2	50·8
Xenon	X	...	128	127
Ytterbium	Yb	...	173·0	171·7
Yttrium	Yt	...	89·0	88·3
Zinc	Zn	**64·91**	65·4	64·9
Zirconium	Zr	...	90·6	89·9

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